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The Effect of S-donor Ligands on the Sensitization of Silver Bromide Crystals with Iridium (III).

Juan A. Zuleta
Rochester Institute of Technology

February 4, 1987

The Effect of S-donor Ligands on the Sensitization of Silver Bromide Crystals with Iridium (III).

by
Juan A. Zuleta
B.S. Universidad de la Salle
Bogota, Colombia
(1984)

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in the Center for
Imaging Science in the College of Graphic Arts
and Photography of the
Rochester Insitute of Technology

February 4, 1987

Signature of the Author _____
Center for Imaging Science

Accepted by _____
Coordinator of the M.S. Degree Program

College of Graphic Arts and Photography
Rochester Insitute of Technology
Rochester, New York

CERTIFICATE OF APPROVAL

M.S.DEGREE THESIS

The M.S. Degree Thesis of Juan A. Zuleta
has been examined and approved
by the thesis committee as satisfactory
for the thesis requirement for the
Master of Science degree

Judith M. Harbison, Thesis Advisor

Paul B. Gilman Jr.

Harry E. Roberts

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Date February 4, 1987

The Effect of S-donor Ligands on the Sensitization of Silver Bromide Crystals with Iridium (III).

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Submitted to the Center for
Imaging Science in partial fulfillment
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Abstract

Different concentrations of potassium thiocyanate (SCN) were used in combination with Iridium (III) hexachloride (Ir) to surface sensitize an octahedral silver bromide emulsion. Surface sensitivity increased by 0.90 log H over the unsensitized emulsion when Ir and SCN were added during sensitization compared to 0.45 log H when the iridium salt was used alone. A decrease of 2.40 log H was observed when an Ir-SCN complex was formed and then added to the emulsion. An increase of 1.05 log H was obtained if gold, thiocyanate and iridium were used. Similar results were obtained using tetramethylthiourea (TMT) or thiodiglycol (TG) instead of SCN. The emulsion was sensitized with S+Au and Au+SCN for comparison. The mechanism of iridium sensitization is discussed based on the experimental results.

ACKNOWLEDGEMENTS

The author wants to express his gratitude to several people who offered their assistance during the preparation and completion of this thesis. Dr. Ingo Leubner and Dr. Paul Gilman, from the Eastman Kodak Research Laboratories for helpful technical discussions, Mr. Rid Tinney from Eastman Kodak for his assistance in the design and construction of the emulsion facilities, Dr. William Jensen, formerly a professor of inorganic chemistry at RIT for his explanations on the thermodynamics and CFSE of inorganic complexes, to Dr. Gordon McDugle from Eastman Kodak for help in the characterization of some of the complexes used in this research, and to Mr. Harry Roberts from R.I.T. for providing references and patent literature. To the late Dr. Ronald Francis for his teaching, encouragement, and help both at the professional and the personal level. A very special note of gratitude to my thesis advisor Dr. Judith M. Harbison from the Eatman Kodak research laboratories for contributing with her knowledge, time, discussions, and continuous support to the success of this research.

Finally thanks to my wife Ana Maria for giving me the motivation during difficult times and for her patience during the long hours of preparation of this thesis.

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DEDICATION

To my late father, Bernardo Zuleta, and

to the late "Doc" Francis.

Thank you both.

1. INTRODUCTION

Noble metals have been used to increase the sensitivity of silver halide crystals since as early as 1896.[1,2] Gold has been by far the most widely used noble metal, but recently platinum metals, and iridium in particular, have acquired special importance as sensitizers. Techniques investigated to use iridium as a sensitizer include doping an iridium(III) complex, generally a hexahalide, into the silver halide crystal in the precipitation stage to increase internal sensitivity, and ripening the emulsion in the presence of an iridium complex to improve surface sensitivity. Several mechanisms have been proposed for the sensitizing action, including hole[3,4,5] and electron [5,6] trapping, transient electron trapping[7], a stabilizing effect against influences of storage,[8] and enhancement of the developability of the latent image after exposure.[9] Direct incorporation of iridium in the latent image has been only mentioned as a possibility worth studying.[8]

In his classic paper, Bahnmuller suggested that iridium(III) can act as a hole trap, while iridium(IV) acts as an electron trap.[5] Sakai and Baba, however, demonstrated that in the presence of excess silver ions, the tetravalent iridium is reduced to trivalent form ,[10] and Pouradier obtained reduction of Ir(IV)

to Ir(III) by gelatin[11]. These data suggest that iridium(III) is the form incorporated as sensitizer of silver halide. EPR studies done on large AgBr crystals at low temperatures indicate that iridium (III) can act as an electron trap by reduction to Ir(II).[12] Leubner found the number of vacancies associated with Ir doping to be only 50% of the expected number and proposed that the sensitizer is an iridium center which is not fully vacancy-compensated and which acts as a transient electron trap without reduction of the iridium(III) ion.[7]

All proposed mechanisms require that the iridium be incorporated into the silver halide lattice and thus, most of the work has been done by doping with the iridium salt during precipitation to obtain internal latent images. Kawijara and co-workers[13] have attempted to obtain sub-surface images by adding the iridium when 80-97% of the precipitation has been completed. No increase in sensitivity is obtained when the iridium complex is simply adsorbed to the surface of the AgBr crystal.[5,7]

Thiocyanate is a silver halide solvent that can etch the AgBr crystal thus facilitating the incorporation of gold(I) ions into the silver halide crystal lattice.[14] In the case of iridium, it could facilitate the incorporation at a required sub-surface level where the latent image could be developed using a conventional low solvent developer.

A significant drawback of iridium as a surface sensitizer is the strong tendency of its ions to form complexes with gelatin.[5] Based on this fact Carroll suggested that iridium could increase the sensitizing effect of gold, not by acting itself as a sensitizer but merely by displacing the gold ions from the gold-gelatin complex[8], in a mechanism similar to the one Faelens found when palladium is used with gold.[15] Removal of the gold ions from the gelatin complex can also be obtained by using complexing agent like thiocyanate in combination with gold;[16] addition of thiocyanate to iridium-gold sensitization could produce an increase in speed due to displacement of gold and possibly iridium ions from their gelatin complexes. If iridium is incorporated as Ir(III), and acts as an electron trap, its effect could be additive to that of gold, since gold increases the sensitivity by enhancing the formation and stability and reducing the critical size of the latent image rather than acting itself as an electron trap.[17,18]

Stability of the iridium hexahalide in solution could also affect its sensitizing properties. It has been determined by spectroscopic studies that an aqueous solution of hexachloroiridate decomposes to form mixed aquo-chloride complexes according to the following reaction:[19,20]

$$(IrCl_6)^{3-} + nH_2O \text{ ---------- } \{Ir(H_2O)nCl_{6-n}\}^{n-3} + nCl^-$$

Although the aquated species can be incorporated into the silver halide crystal[11], the degree of hydration during sensitization is difficult to determine and the effect of the different aquated forms is not known. If iridium is used in conjunction with thiocyanate ions, there is the possibility of formation of iridium-thiocyanato complexes that could be stable to aquation and complexation by gelatin.

Thiocyanate can also reduce trivalent gold to univalent, being oxidized to thiocyanogen.[21] The univalent gold can be incorporated in a lattice or an interstitial position in the silver halide matrix. Since the first ionization potential of iridium is very similar to that of gold [22], iridium could produce a similar stabilizing effect if it were incorporated in the latent image. It has been also shown that a silver-gold center is a better nucleus for electrolytic deposition of silver than a silver center.[23,24] Although it has been reported that iridium forms solid solutions with silver, the efficiency of an Ir-Ag center as a catalyst for development is not known.

To obtain an Ir^{o} nucleus upon exposure, the Ir(III) ion would have to be reduced to the monovalent state. It has been shown that Ir(I) is one of the two most stable oxidation states for iridium,[25] and that it can be prepared by reduction of Ir(III) in the presence of the appropriate ligand. According to the HSAB criterion for determining the feasibility of

compounds, an Ir(I) thiocyanato complex would be thermodynamically possible,[26] although it has not been reported.

Although the information about complexes of iridium with thiocyanate is scarce, and specific data such as stability constants of the thiocyanate and gelatin complexes are lacking in the literature, it is mentioned that the Ir(III)-SCN complex exists as a thermodynamically stable species, and that it can be prepared from the hexachloride complex by addition of thiocyanate ions,[19,20,25,27] . These data indicate that thiocyanate forms a stronger complex with iridium(III) than the hexahalide.

The present work studies the complexes of iridium with thiocyanate and other S-donor ligands, and the reactions of these complexes as well as the hexachloride complex with water and gelatin using UV-Visible spectroscopy. The sensitization effects of these complexes are determined and compared to that of sulfur-gold, and sulfur-gold-thiocyanate sensitization, and to the sensitization produced by the simple addition of thiocyanate and iridium salts to a silver bromide emulsion during chemical ripening. The additivity of iridium to gold sensitization is tested by comparing the iridium-thiocyanate with iridium-gold-thiocyanate sensitization.

2. EQUIPMENT AND MATERIALS

IBM UV-Visible spectrophotometer model 9420

Magni-Whirl constant temperature bath

Lauda constant temperature bath model RC20

Orion pH and mv meter model 701

Corning pH and mv meter model 140

Orion multiple electrode switch box model 605

Barrington Industries turbine model CJTWO

Premier Mill Corporation dispersator series 2000

Cole Parmer Masterflex pumps with 7013 series heads

Kodak sensitometer model 101

EG&G sensitometer model mark VII

Film sample coater

Silver nitrate Eastman Kodak emulsion grade

Potassium bromide Polaroid Corporation emulsion grade

Phthalated (PA) gelatin Polaroid Corporation emulsion grade

Potassium hexachloroiridate(III) purified by Eastman Kodak (Ir)

Potassium thiocyanate Baker reagent grade (SCN)

Potassium chloroaurate solution supplied by Eastman Kodak (Au)

Sodium thiosulfate pentahydrate Baker reagent grade (S)

Tetramethylthiourea Eastman reagent grade (TMT)

2,2'-Thiodiglycol Aldrich chemical reagent grade (TG)

3. EXPERIMENTAL

3.1. Preparation and Spectroscopic Analysis of Ir compounds

The iridium solutions were prepared directly from the reagent immediately prior to their use to minimize aquation. The Ir-SCN Ir-TMT and Ir-TG complexes were prepared by adding 50mg of the iridium(III) hexachloride to 500 mg of molten ligand. Another set of samples was prepared by adding iridium(III) hexachloride to a 2M solution of the ligand and heating the mixture at 100°C for 2 min. Also, the iridium hexachloride solutions were heated for 24, 48 and 120 hours at 50°C, and the spectra of the resulting solutions were measured and compared to spectra from previous reports on aquation of iridium complexes. Both the iridium chloride and the iridium thiocyanate complexes were added to a warm gelatin solution and the spectra were measured against a gelatin blank. All spectra were measured at 25°C.

3.2. Emulsion preparation

The maximum efficiency of S+Au sensitization has been obtained on (111) surfaces [28], therefore a monodisperse octahedral AgBr emulsion was chosen for this study.

Emulsion #1

0.5N solutions of potassium bromide (solution A) and silver nitrate (solution B) were added simultaneously to 1500 ml of a 0.084N solution of potassium bromide containing 40.0 g of PA gelatin (solution C). The concentration of free Ag^+ ion was measured with an Orion 701 potentiometer using a silver bar coated with silver bromide as the specific ion electrode and a Ag/AgCl reference electrode, and controlled with a third jet that was 0.10M KBr. The conversion from absolute mv to pAg was calculated using the Nernst equation

$$E = E^o + \frac{RT}{nF} \log [Ag^+] - E_{ref}$$

$$E = E^o - \frac{RT}{nF} pAg - E_{ref}$$

$$E = E^o - \frac{RT}{nF} (pKsp-pBr) - E_{ref}$$

Where $E^o = 799$ mv
$E_{ref} = 222.3$ mv
$[Ag^+]$ = analytical concentration of silver ion

The calculated value for E was -66.1 mv and pAg was 9.53 at 70°C. The diagram for the precipitation is shown in fig 1. The rate of addition of the two solutions was 12.5 ml/min for a total run time of 60 min.

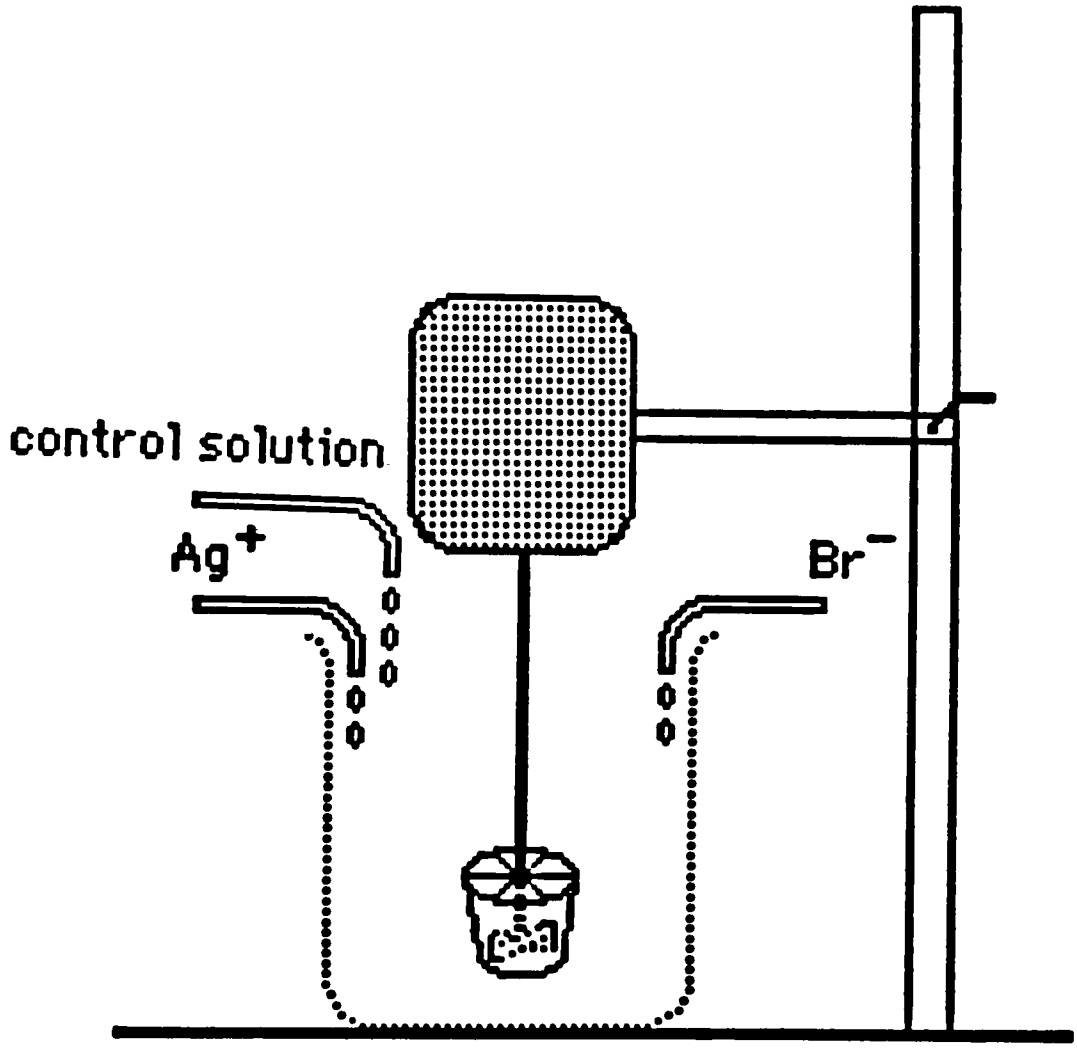


Figure 1. Equipment set-up for precipitation of emulsion #1.

Electron micrographs of the emulsion showed a relatively large number of tabular grains , as well as needles, with some octahedral and a few cubic grains present.

Several causes were identified for the failure of this first trial. The concentration of the KBr control solution was too close to that of the initial bromide solution and therefore, a relatively large amount had to be used to keep the pAg constant resulting in a significant increase in volume. The agitation system proved to be very inefficient and local areas of relatively high concentration of silver and bromide were present near the two jet streams. This resulted in different degrees of supersaturation in these areas as well as in different pAg conditions causing the different crystal habits. The inefficient agitation system also resulted in a large amount of foam being formed on the surface of the emulsion. Since the two jets were surface delivered, this also contributed to decrease the rate of mixing of the silver and bromide ions.

The calculations for pAg and electrochemical potential were also found to be incorrect, since the ionic strength and temperature coefficients were not included in the calculations of Ksp, pBr and pAg and the calculated E_{cell} from the Nernst equation. The value for the Ag/AgCl reference electrode used was obtained from chemical tables[29], and did not correspond to the concentration of the filling solution actually used by the

manufacturer. The fact that the electrode was placed directly into the solution at 70°C and the value for Eo was taken at 25°C increased the error in the calculations.[30]

Emulsion #2

A second emulsion was precipitated using the same concentrations of solutions A and B as used in emulsion #1. Solution C was 0.012N KBr containing 12.5g of PA gelatin. The calculated pAg was 8.35 at 70°C, and the vAg 22±5 mv. The two jets were surface delivered and foam was controlled by spraying the emulsion with a mixture of secondary and tertiary butyl alcohols. The agitation system was changed to the Premier Mill dispersator; a propeller with three vertical blades was used instead of the turbine, and a 0.1N KNO_3 solution was used as a salt bridge between the reference electrode and the emulsion as shown in fig 2. The delivery rate for the silver pump was maintained at 12.5ml/min and the rate of delivery for the bromide pump was calculated to obtain a constant free bromide ion concentration throughout precipitation. The calculations are shown in page 13.

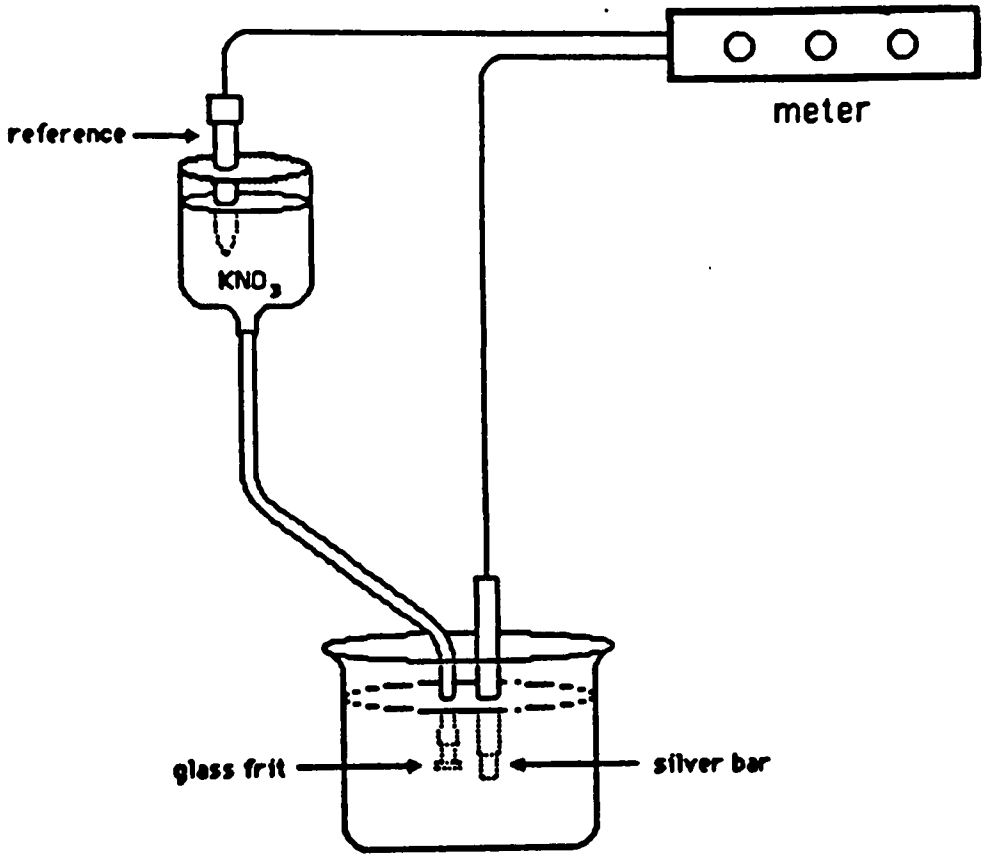


Figure 2. Electrode and salt bridge assembly.

Vi = initial volume of Br + gel solution (sol C)

Ci = concentration of initial solution

Xi = # moles of Br in initial solution

Va = volume of solution A added

Xb = # moles of Br added

Vb = volume of solution B added

Xa = # moles of Ag added

Cb = concentration of the bromide jet

Since at any point the excess of Br ion has to be constant

$$C = Ci = \frac{\text{total \# of moles of Br}}{\text{total volume of solution}}$$

$$C = \frac{Xi + Xb - Xa}{Vi + Vb + Va} = \frac{Xi + VbCb - Xa}{Vi + Vb + Va}$$

$$Vb = \frac{CiVa + Xa}{Cb - Ci}$$

$Rb = Vb/t$ where t = time of precipitation

In order to prevent a large increase in volume $Cb > Ci$

The pAg and vAg (electrochemical potential) were recalculated using the corrected Nernst equation

$$vAg = E_{Ag} - E_{ref} .$$

$$E_o = \frac{\Delta H - T\Delta S}{nF} .$$

This is aproximated by the empirical equation [31]

$$E_o = 799 - 0.1(t-25)$$

$$E_{Ag} = 799 - 0.1(t-25) - \frac{RT}{nF} pAg$$

where $RT/F = 0.1984(t+273.15)$ mv

$pAg = pKsp - pBr$ and $pBr = -\log (\&Br\{Br^-\})$

$$pKsp = 12.126 - 5868/T - 0.015953T$$

$$\ln \&Br = \frac{-A*I^{1/2}}{1 + I^{1/2}} + 0.22(I)$$

$$A = 1.1327 + 1.50563*10^{-3}t + 1.16836*10^{-5}t^2$$

A = Debye-Huckel constant
I = ionic strength
T = absolute temperature
t = temperature in celsius
&Br = activity of the bromide ion
E_{ref} = 197 mv

Electron micrographs showed a much higher degree of monodispersity, but approximately 50% of the observed grains were tabular. This was attributed to the surface delivery of the jets which again produced a large decrease in the reaction rate, resulting in local inhomogeneities.

Emulsion #3

The experimental layout was identical to emulsion 2 but the jets were delivered to the bulk of the emulsion using silicon tubing and a baffle was introduced in the beaker to increase mixing rate (fig 3). The emulsion obtained was octahedral with approximately 20% of tabular grains. The results were attributed again to inefficiency in the mixing due to the flexibility of the silicon tubing which combined with the high agitation rate prevented the delivered solutions from being mixed with the bulk of the solution in a short enough time to provide homogeneity in the degree of supersaturation and the pAg in the bulk of the emulsion.

Emulsion #4

The emulsion was precipitated under the same conditions of emulsion #3 but the position of the two streams was fixed by welding two pieces of stainless steel tubing to the wall of the vessel. The dispersator was located so that the propeller was 2 cm away from the middle point between the two jets (fig. 4).

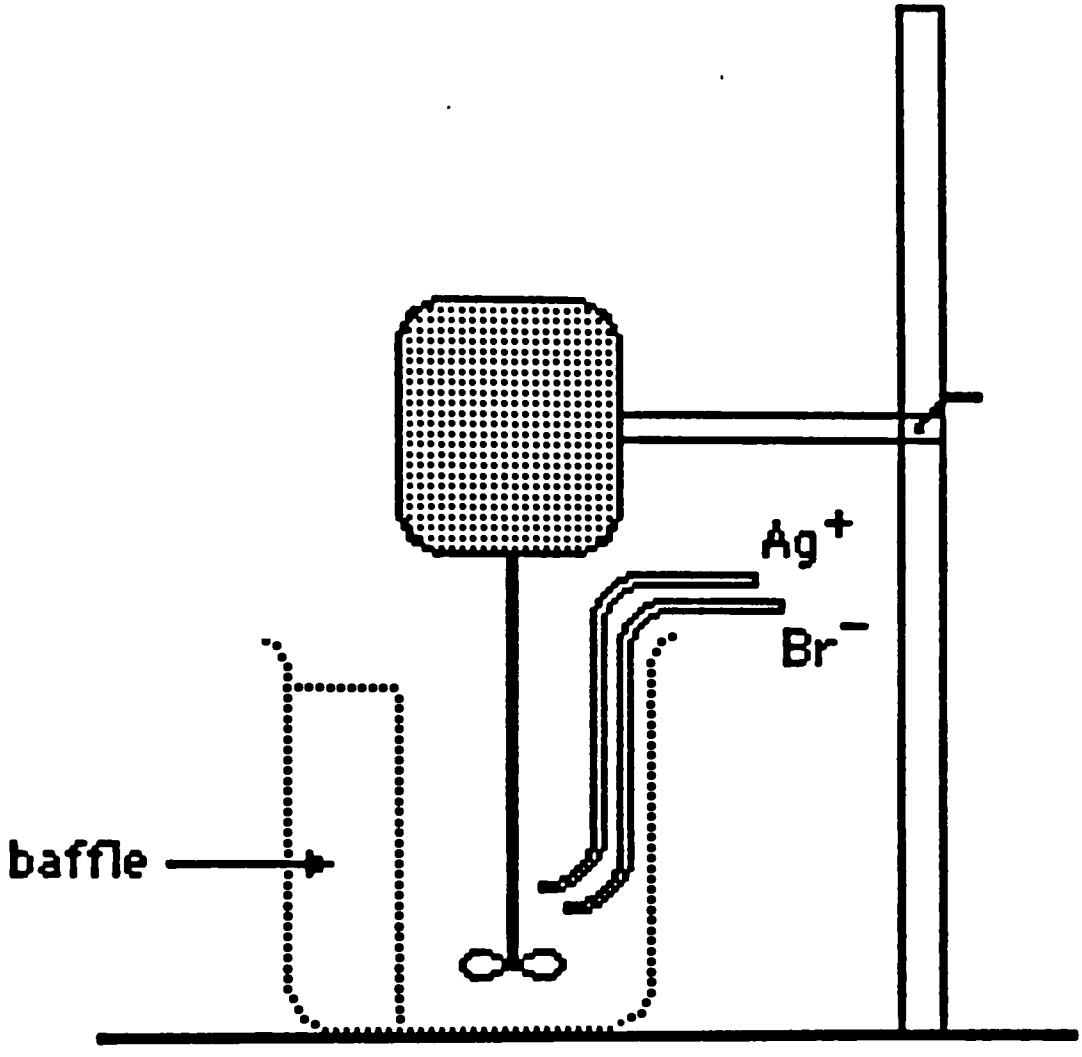


Figure 3. Delivery and agitation system for precipitation of emulsion #3.

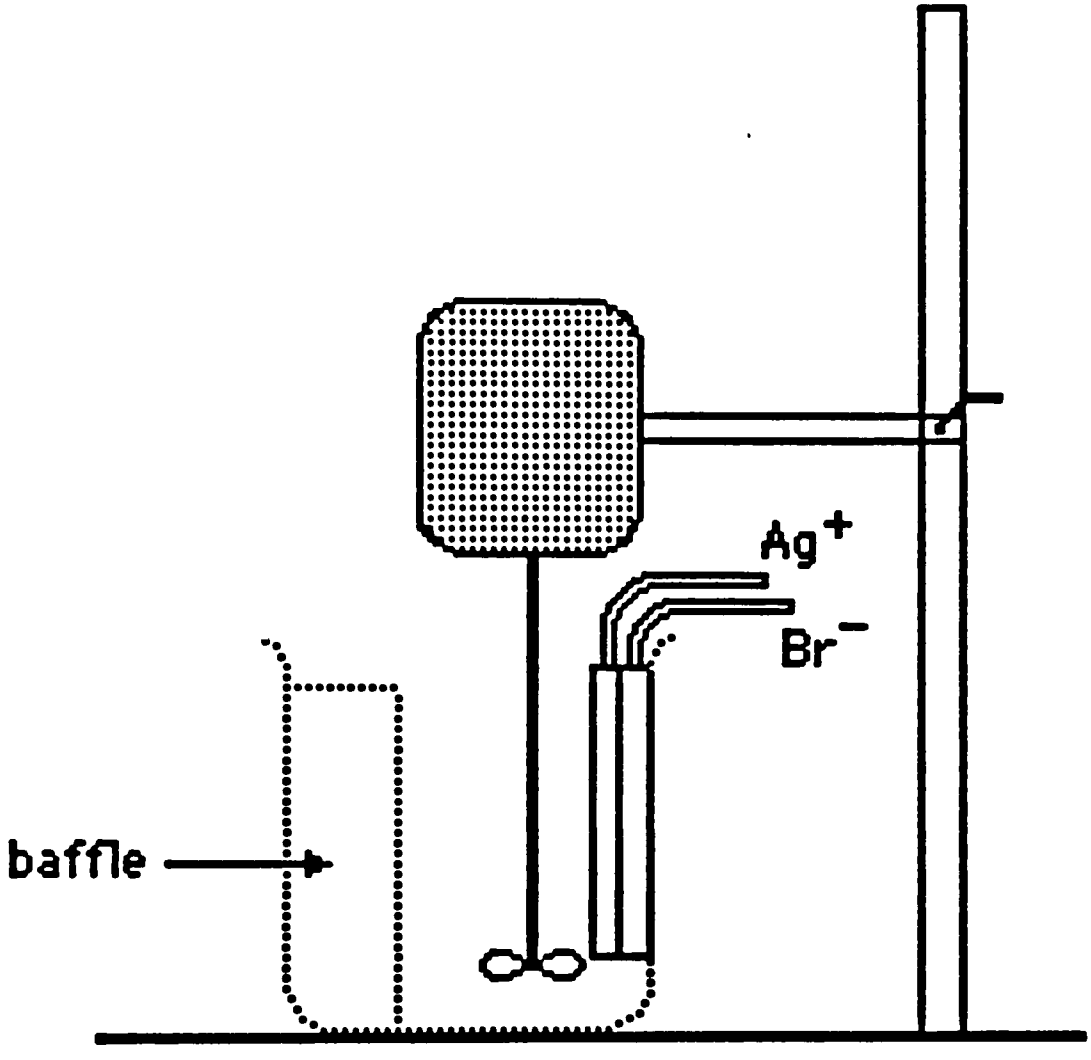


Figure 4. Delivery and agitation system for precipitation of emulsion #4.

Precipitation was started at a rate of 2 ml/min, increased to 40 ml/min over 25 minutes and kept at that fixed rate for 25 minutes to obtain a total precipitation time of 50 min. The pBr was kept constant by increasing or decreasing the bromide pump rate. A multiple electrode switch box connected to a Corning 142 meter was used to monitor pH and absolute mv (vAg) simultaneously. The emulsion obtained was a highly monodisperse octahedral emulsion with a mean grain diameter of 0.4u and the grain size frequency distribution shown in figure 5.

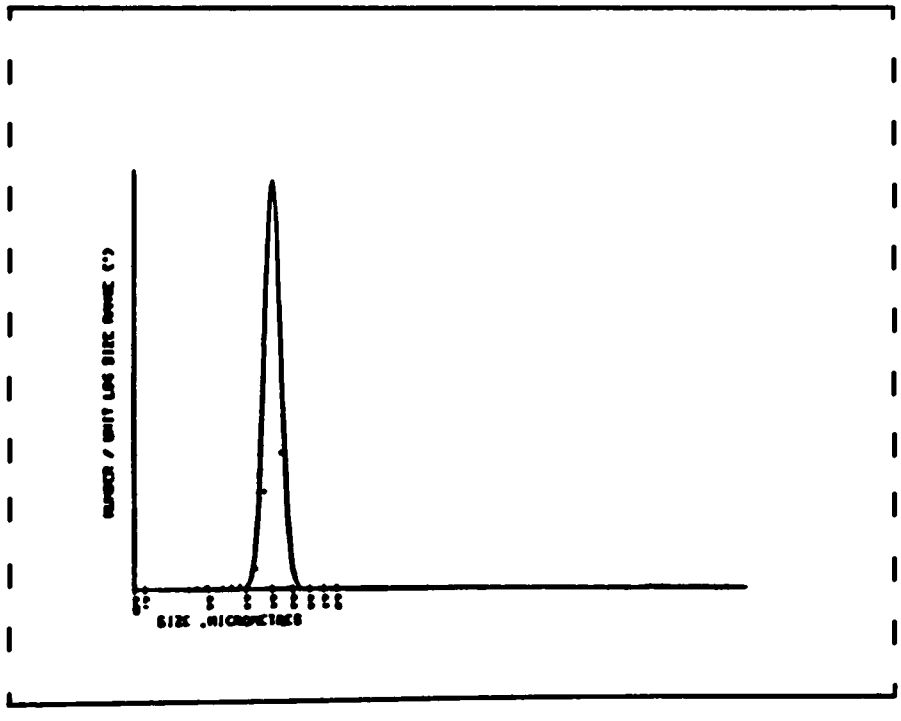
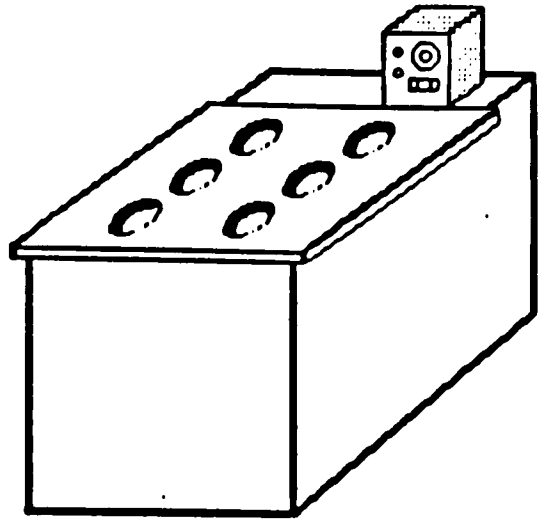


Figure 5. Grain size frequency distribution of emulsion #4

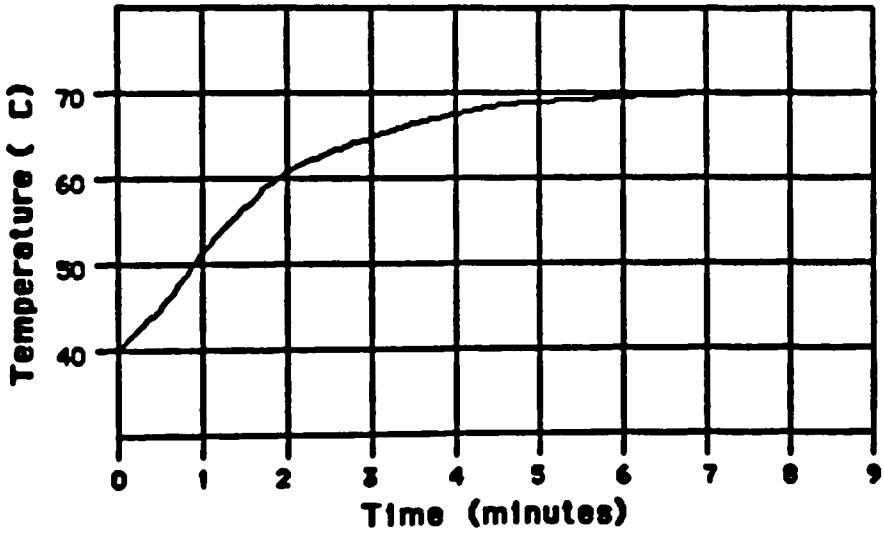
3.3 Sensitization

The emulsion used was a 0.4u octahedral made by the doublejet method; pAg was adjusted to 8.0 and pH to 6.5. An optimum sensitization for sulfur and gold was determined by running five concentration combinations of sodium thiosulfate (S) and potassium chloroaurate (Au) for 10, 20, 30, 50 and 70 minutes at 70°C, as shown in fig 7a. The sensitizers were added at 40°C, agitated for three minutes and then the beakers were transferred to a water bath at 70°C (T); Plots of temperature vs time between 40 and 70°C were obtained for six different beaker placements in the water bath at T by using a chart recorder connected to a thermometer. The probe was immersed in a sample of 25 ml of emulsion in the beaker (fig 6). The average time to reach T was determined to be 6.4 min with a standard deviation of 0.33 min.

Using the same experimental design, different levels of iridium hexachloride and potassium thiocyanate were used to sensitize 28g portions of the emulsion (fig 7b). The emulsion was diluted 1:7 with a 7% gelatin solution before coating to obtain 100mg of Ag/ft^2. A second sensitization series was done in which the dilution with 7% gelatin was done before sensitization. Three coatings were made from each sample to minimize variations due to thickness of the coating.

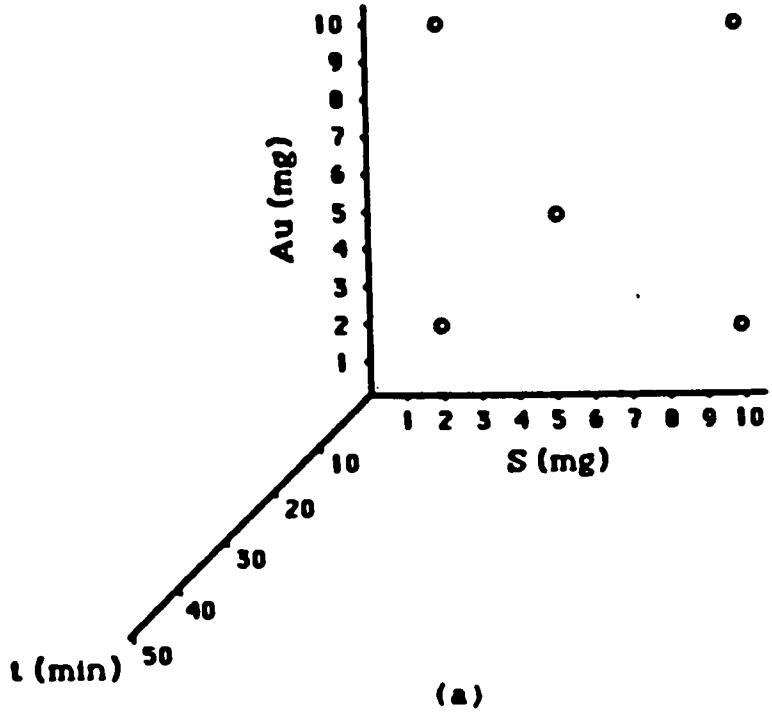


(a)

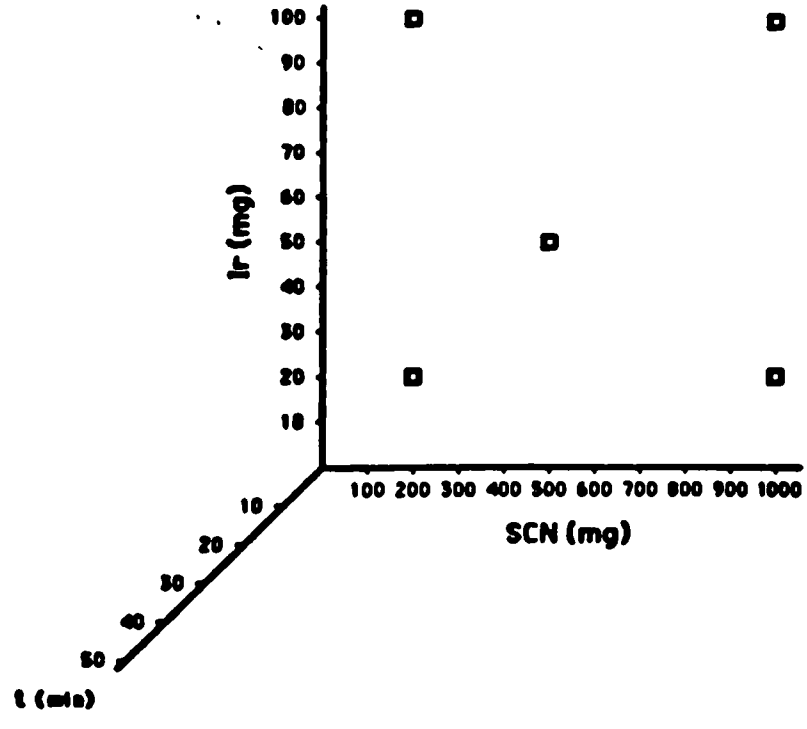


(b)

Figure 6. (a) Water bath design for simultaneous sensitization of 6 emulsion samples. (b) tipical T vs time profile.



(a)



(b)

Figure 7. Factorial experimental design for (a) S+Au and (b) Ir+SCN sensitization

The additivity of iridium and gold sensitization in the presence of thiocyanate was tested using three 28g samples of emulsion sensitized with Ir+SCN, Au+SCN, and Ir+Au+SCN. A sample of emulsion containing only SCN was used as control.

The samples were exposed using an EG&G Mark VII sensitometer, where exposure was 52 lux-sec at 10-3 sec, and developed in Kodak D-72 (a low solvent developer) for 2 minutes at 20°C. The strips were read in an ESCO speedmaster densitometer, and speed was determined for a density of 0.3 above base+fog.

A comparison of the latent image keeping characteristics of the sensitized emulsions was made: Similarly exposed samples of the S+Au and Ir+SCN sensitized emulsions were kept in an oven a 50°C and 100% humidity for 3 weeks and then processed as described above. A similar set of samples was exposed, then treated before processing with a bleaching solution[32] composed of 3.0 g potassium ferricyanide, 12.5 g phenosafranine and water to make 1.0 liter.

The Ir-SCN, S-Au, and unsensitized emulsions were also tested for solarization: an open gate exposure of 52 lux seconds in the EG&G sensitometer was followed by a lower intensity (1700 lux) exposure though a step tablet in a Kodak 101 sensitometer.

4. RESULTS AND DISCUSSION

4.1 Spectroscopic Analysis

The spectra of the iridium complexes were compared to those obtained by Jorgensen[33], Chang,[34] and De Haas,[35]. The results for the hexahalide and the thiocyanate complexes as well as for the different aquated species correspond to those reported in the literature. The different spectra for the iridium hexachloride in aqueous solution have been assigned to different degrees of aquation. The shift and change in intensities of the two absorption peaks at 355 and 415 nm characteristic of the hexachloroiridate(III) ion has been attributed to a substitution of one of the chloride ligands by a water molecule (fig 8)

In the presence of a high concentration of thiocyanate ions, the two peaks dissapear and a long band that extends into the deep UV is obtained. Although no spectral features are observed, this spectrum which is shown in fig 9, corresponds to that reported for the hexathiocyanatoiridate (III) ion.[35] This complex was further characterized by comparing its IR spectrum to that of an iridium thiocyanate complex prepared and isolated by the method described by Schmitke[27], and characterized using elemental analysis.

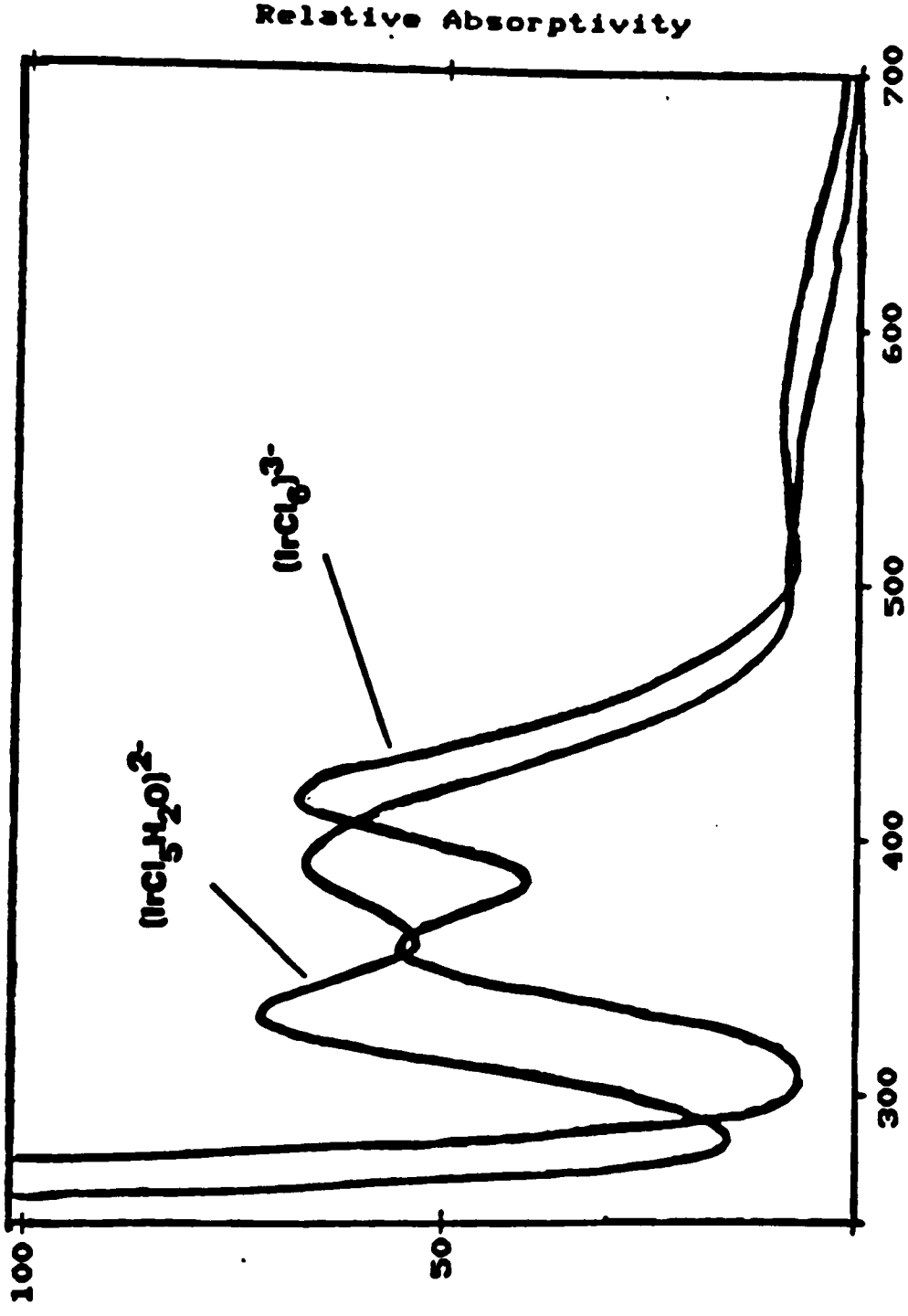


Figure 8. Spectra of $IrCl_6$ and $IrCl_5H_2O$

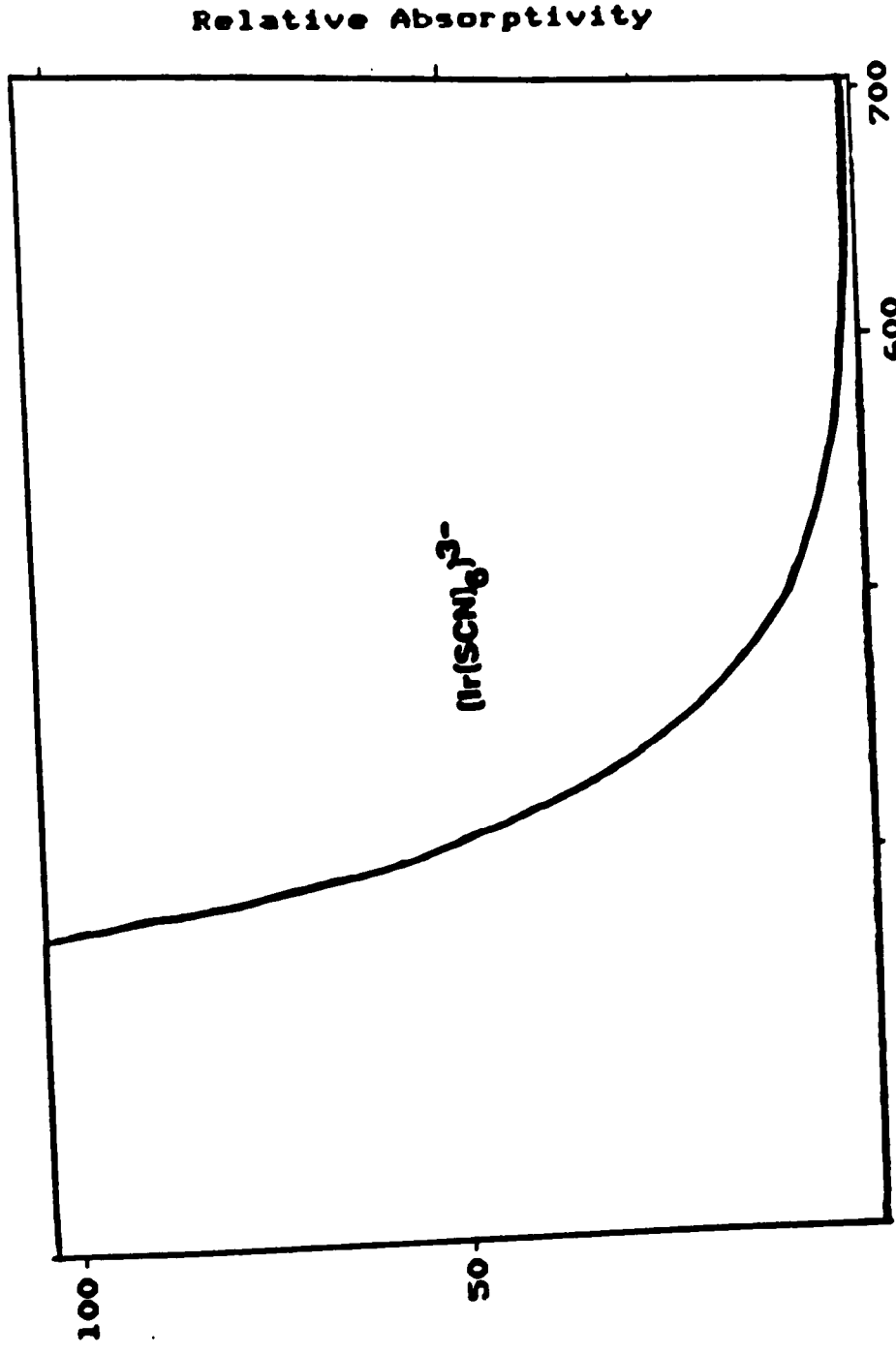


Figure 9. Spectrum of $Ir(SCN)_6$

When the iridium hexachloride and thiocyanato complexes were highly diluted, the hexachloride decomposed to give the mono-aquated species and upon heating at 50°C suffered further aquation to give a spectrum that is similar to that reported for the tris-aquo complex $K_3IrCl_3(H_2O)_3$. The spectrum of the thiocyanato complex did not change even when the complex was highly diluted and was heated at temperatures as high as 80°C.(fig 10)

The spectra obtained for the Ir-TMT and Ir-TG complexes shown in fig 11 could also be attributed to total or partial substitution of the chloride ligands by a TMT or TG ligand to form a compound of the type $IrCl_{6-n}L_n$.[36,37] The spectra of these complexes was also found to be stable when the solutions were diluted and heated at relatively high temperature.

A similar situation occurs when the complexes were dissolved in gelatin: the halide complex shows a decrease in the intensity of the two absorption peaks at 355 and 415 nm and an increased absorption below 310 nm suggesting complexation by the gelatin (fig.12) The thiocyanate containing solution gave the same spectrum in gelatin and in aqueous solution, (fig.9 and 13). When the gelatin solutions were heated, the halide gave a spectrum that corresponds to that of the tris-aquo species while the thiocyanate was again unchanged (fig 13). The samples made from molten and 2M aqueous SCN gave identical spectra.

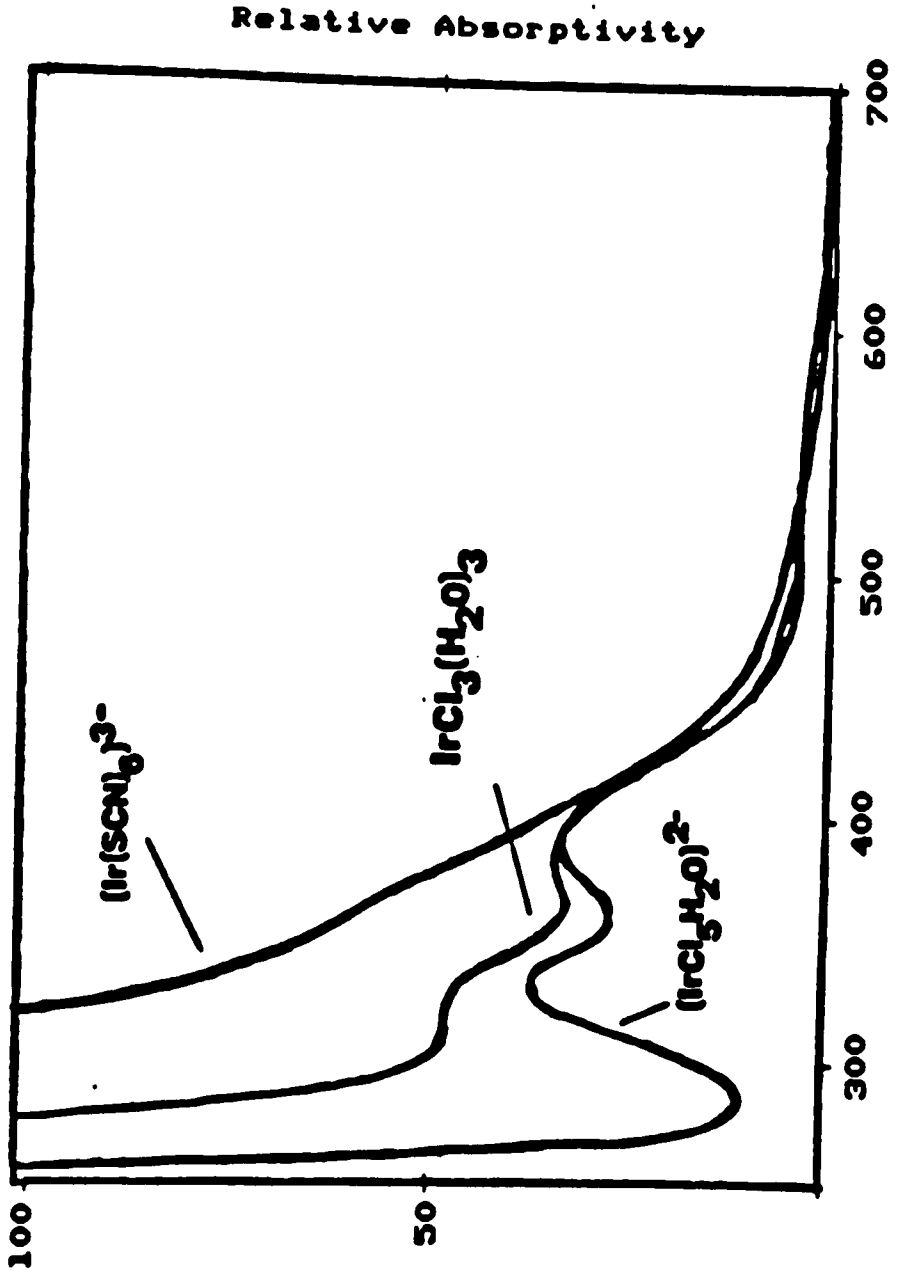


Figure 10. Spectra of $IrCl_5H_2O$ $IrCl_3(H_2O)_3$ and $Ir(SCN)_6$

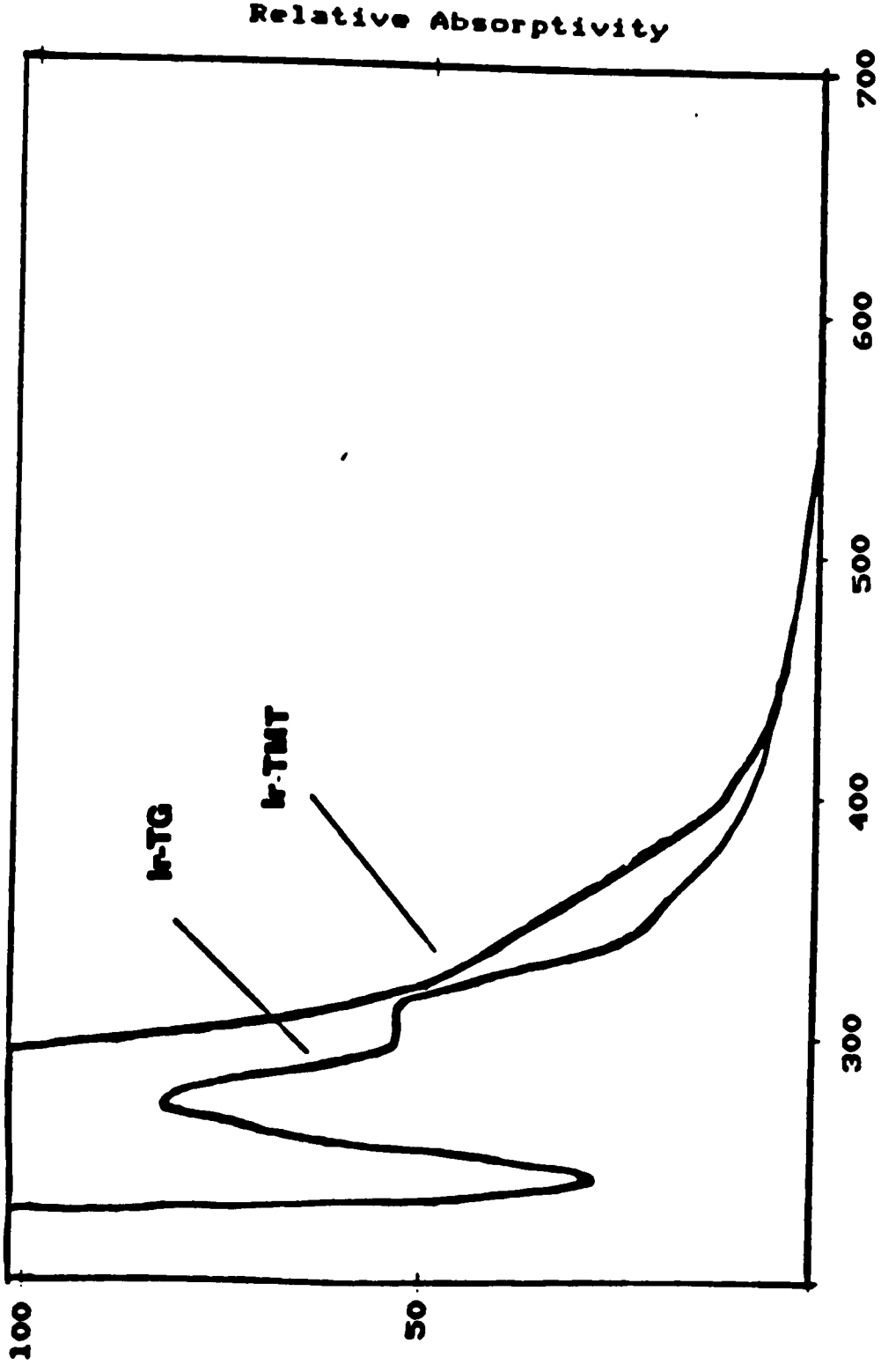


Figure 11. Spectra of IrTMT and Ir-TG complexes

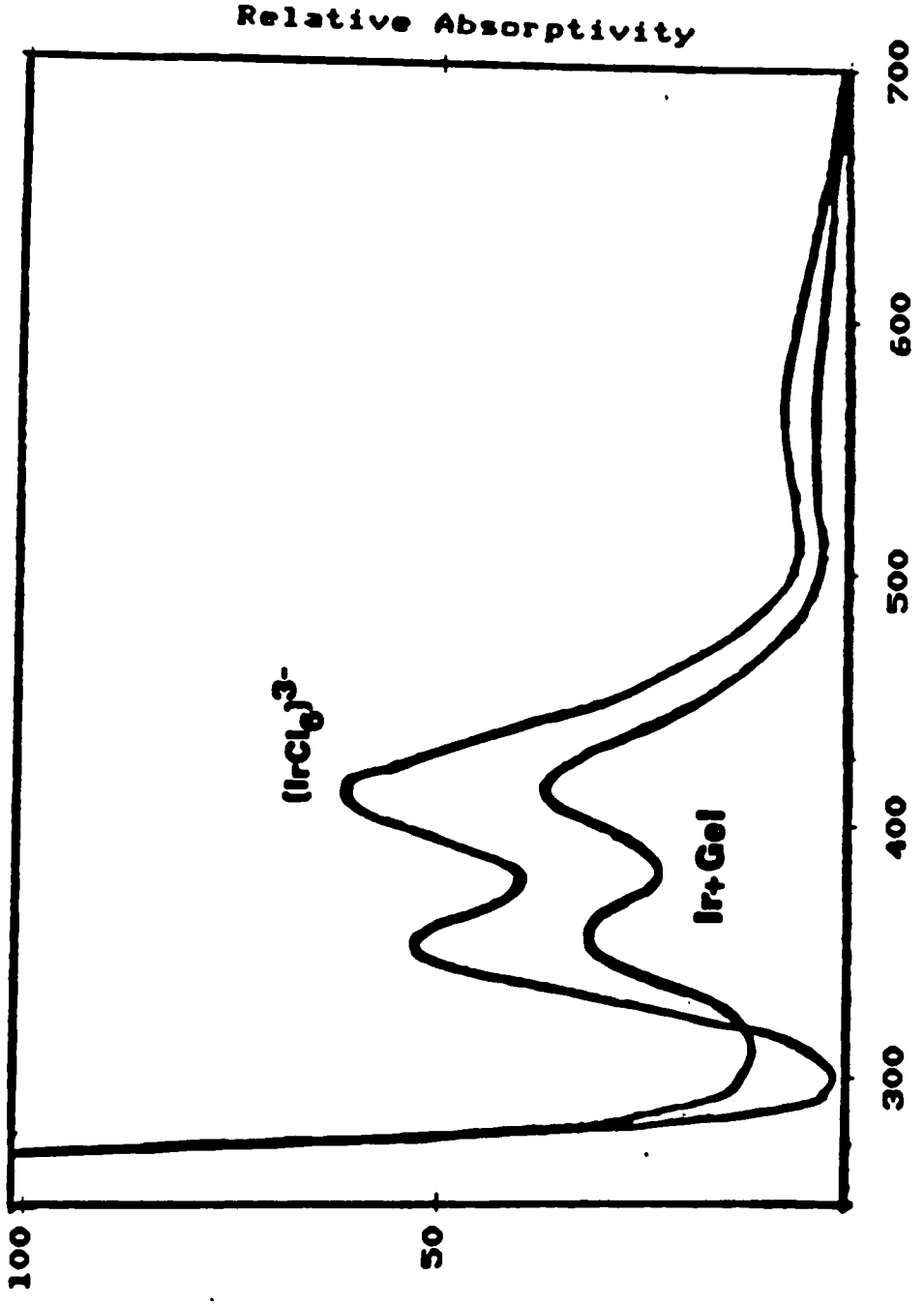


Figure 12. Spectra of $IrCl_6$ and Ir-Gel complexes

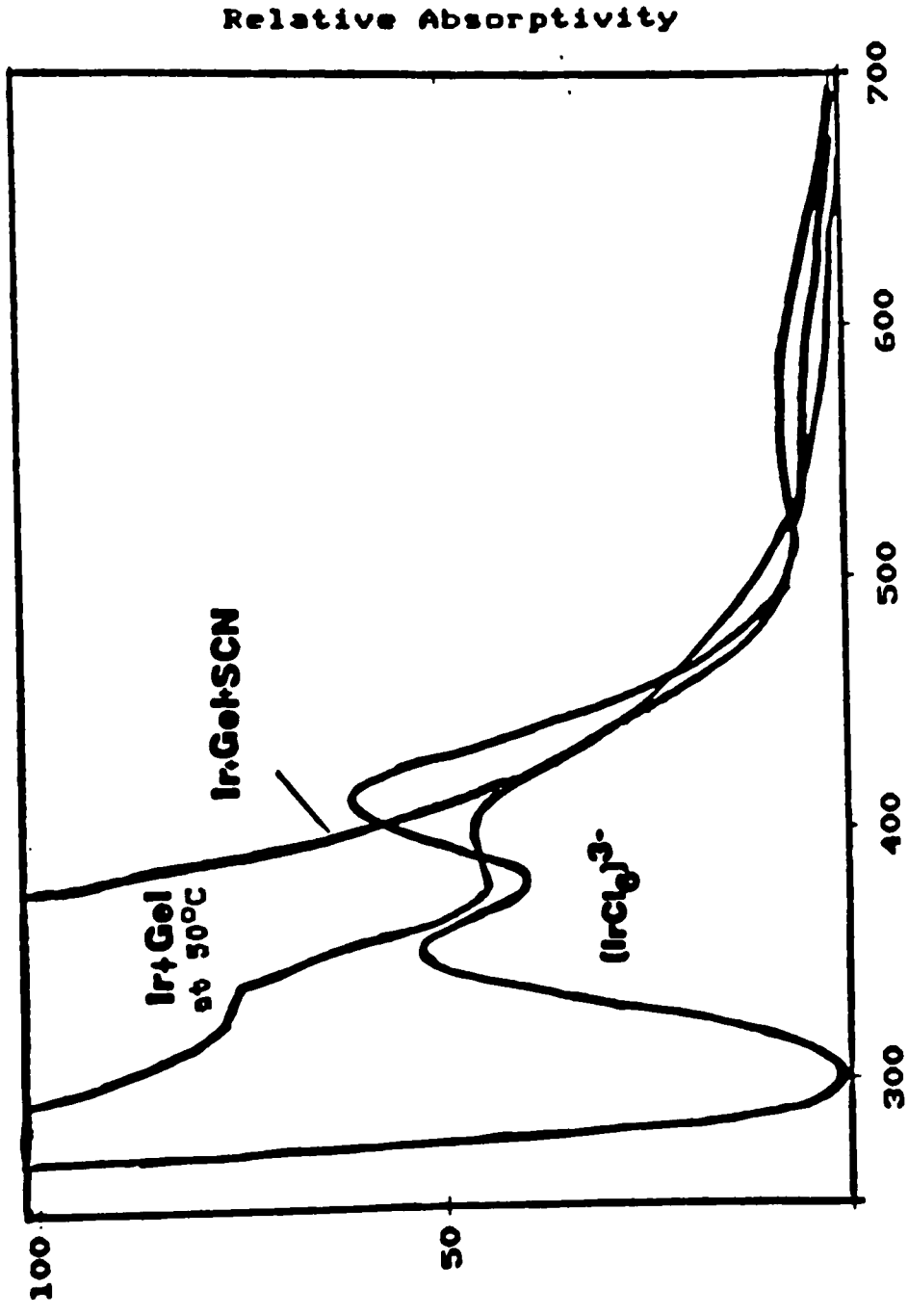


Figure 13. Spectra of $IrCl_6$, Ir-Gel, and $Ir(SCN)_6$ -Gel complexes

The analysis of the spectra obtained suggests that the order of increasing stability of the complexes is $Cl < Gel < H_2O < SCN$. This accounts for the instability of the $IrCl_6^{3-}$ in solution and also suggests that the efficiency of Ir(III) as a surface sensitizer may be diminished by its complexation by gelatin. Because of its apparent higher stability, the thiocyanato complex may not undergo aquation, nor form the gelatin complex. But at the same time, if the Ir-SCN complex is formed before sensitization, the thiocyanate ions may be less readily displaced from the complex than the chloride ions. There is a strong possibility that the iridium may be associated with the silver halide matrix as $Ir(SCN)_6^{3-}$, rather than as the halide complex.

4.2 Sensitization

The best sulfur-gold sensitization was obtained when 2 mg S and 2 mg Au/mol AgBr were used and the sample was heated for 20 minutes at 70°C. A speed increase of 1.5 log H was obtained. This is consistent with the results of Marchetti et al [29] and Harbison [38]. When 200 mg SCN/mol AgX was used in combination with the sulfur and gold, only a 1.35 log H increase was observed. Larger concentrations of thiocyanate produced even smaller increases in speed.

When 20 mg of the iridium(III) hexachloride/mol AgX was used alone and the emulsion was heated for 10 min., a very small increase in speed (0.30 log H) was obtained relative to the unsensitized emulsion. Extending the sensitization time to 50 min. did not produce any significant increase in speed.

Increasing the amount of iridium to 50mg/mole AgX produced only a slight further speed improvement (to 0.45 log H), while at higher concentrations less increase in speed was observed. With the simultaneous addition of 200 mg of thiocyanate and 20 mg of Ir(III)/mole AgX to the unsensitized emulsion a significant improvement in speed and contrast (0.6 log H compared to the above 0.30 log H) was obtained over the use of the iridium hexachloride alone. Increasing the ratio of SCN/Ir did not produce any further improvements. The best sensitization (0.9 log H increase) was obtained when 500 mg of SCN and 50 mg of Ir/mol AgX were used. Again, higher concentrations of the sensitizer resulted in slightly less increase in speed; fig 14 shows the characteristic curves for the unsensitized, and the optimum Ir and Ir+SCN sensitized emulsions.

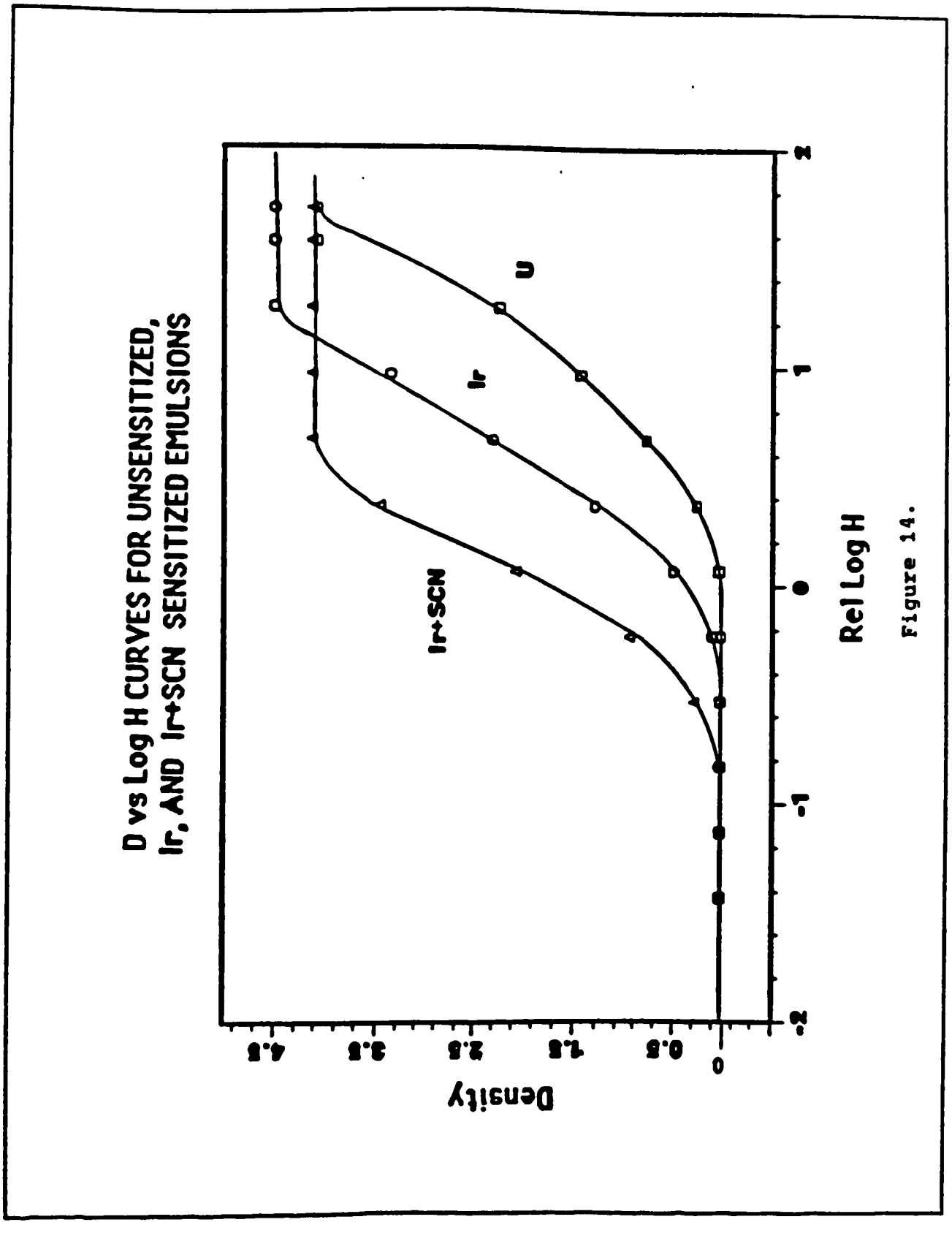

D vs Log H CURVES FOR UNSENSITIZED,
Ir, AND Ir+SCN SENSITIZED EMULSIONS
Density
0
0.5
1.5
2.5
3.5
4.5
-2
-1
0
1
2
Rel Log H
U
Ir
Ir+SCN

Figure 14.

When the Ir-SCN complex was pre-formed and 20 mg of the complex + 200 mg of thiocyanate/mol AgX was added to the emulsion, a strong desensitization (down to -2.4 log H relative to the unsensitized emulsion) was observed. The effect was more evident as the ratio of Ir-SCN/SCN decreased. fig 15 shows the characteristic curves for the unsensitized, and the Ir+SCN and $Ir(SCN)_6^{3-}$ sensitized emulsions.

The use of TMT and TG produced an increase in the sensitization effect of Ir(III) when compared to that of the iridium alone. The speed obtained was similar to the best obtained with SCN (fig 16). The pre-formed Ir-TMT and Ir-TG complex also acted as strong desensitizers.

The proposal that the Ir(III) complex has to be incorporated into the lattice to act as a sensitizer was made by Bahnmuller[5] and more recently by Leubner.[7] From the sensitometric data it is obvious that the thiocyanate ion is needed for the optimum surface sensitization with Ir(III), and it is also obvious that the mode of addition of the ions has a definitive influence on the sensitivity of the emulsion. The effect of the changes in concentration of the two ions, however, is not as clear.

When the Ir and the SCN are added simultaneously during chemical sensitization, the thiocyanate ions may etch the surface of the AgBr crystal. The substitution reaction replacing silver

and bromide ions in the crystal with the iridium hexachloride may be promoted and the incorporation of the complex into the crystal at the surface or sub-surface level may be facilitated. This incorporation can explain the increase in speed that is obtained when the emulsions are processed in a low solvent developer.

The similarity of the results produced by SCN, TMT, and TG also supports the hypothesis for the need of incorporation of the complex in the AgX matrix. The small increase obtained by Ir alone can be explained if one considers that the samples were heated at 70°C for 20 min. and some ripening is likely to occur which allows a small amount of Ir to be built into the AgBr matrix.

The addition of gold to the iridium+thiocyanate sensitization produced a greater increase in speed (1.05 log H). This suggests thst there there is additivity of iridium and gold sensitization since the emulsion sensitized with only gold and thiocyanate showed an increase in speed of only 0.6 log H and the emulsion with thiocyanate alone did not show any speed increase compared to the unsensitized emulsion. Figs. 17-18 show the D-log H curves for the unsensitized, as well as the S-Au, Ir, Ir+SCN and Ir+SCN+Au sensitized emulsions.

The relative log H increases in speed for the Ir, Ir+SCN, Ir+TMT, Ir+TG, S+Au, Au+SCN, and Ir+SCN+Au are shown in Table I.

Diluting the emulsion 1:7 with a 7% gelatin solution before sensitization caused the increase in sensitization to be only 0.45 for the Ir+SCN and 0.15 for the Ir alone; the S+Au sensitized emulsion showed the same increase in speed as when diluted prior to coating (table II).

The decrease in sensitization efficiency observed upon increasing the Gel/AgX ratio suggests complexation of the iridium by gelatin. Displacement of the Ir(III) from its gelatin complex by thiocyanate can only be accomplished if an iridium-thiocyanato complex is formed. Stabilization of the hexachloride complex against aquation by thiocyanate can also be obtained only by the formation of an Ir-SCN complex. Premixing the iridium and the thiocyanate gave a compound that acted as a desensitizer. Therefore, it is believed that the Ir-SCN complex is not formed during the sensitization treatment.

Both the unsensitized and the Ir+SCN sensitized emulsions solarized under the exposure conditions used in this work. The degree of solarization was higher for the Ir+SCN sensitized emulsion.

TABLE I

Relative Increase in Sensitivity

S	Au	Ir	SCN	TMT	TG	AS
2	2	--	---	---	---	1.50
2	2	--	500	---	---	1.35
-	-	50	---	---	---	0.45
-	-	50	500	---	---	0.90
-	-	50	---	680	---	0.90
-	-	50	---	---	630	0.90
-	2	50	500	---	---	1.05
-	2	--	500	---	---	0.60
-	-	--	500	---	---	0.00

TMT - tetramethylthiourea
TG - thiodiglycol

TABLE II

Effect of Gel/AgX ratio on sensitization

Dilution	S+Au	Ir+SCN	Ir
Undiluted*	1.50	0.90	0.45
Diluted 1:7	1.50	0.45	0.15

* Diluted 1:7 with 7% gel before coating

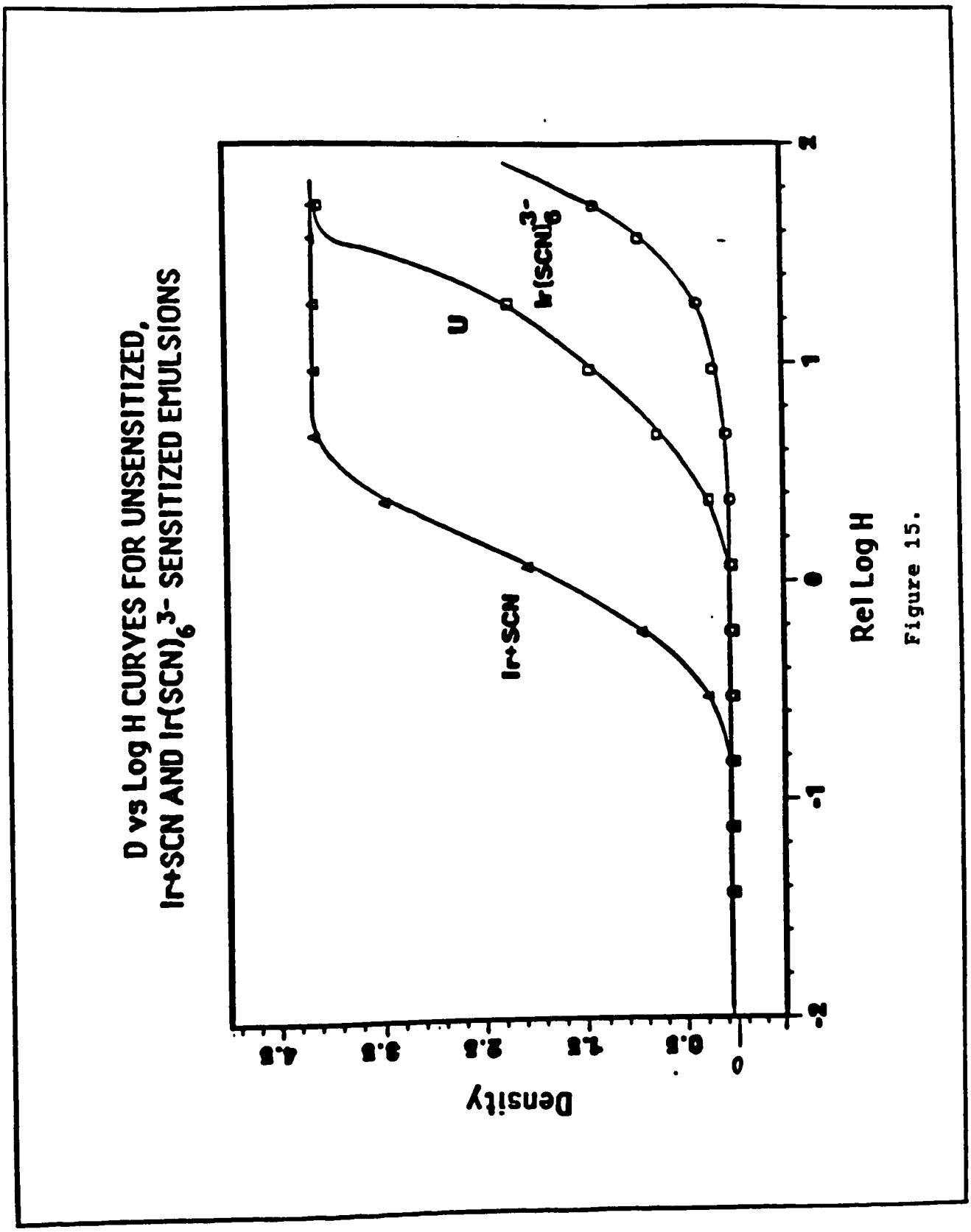

D vs Log H CURVES FOR UNSENSITIZED,
Ir+SCN AND Ir(SCN)$_6^{3-}$ SENSITIZED EMULSIONS
Density
0
0.5
1.5
2.5
3.5
4.5
-2
-1
0
1
2
Rel Log H
Ir+SCN
U
Ir(SCN)$_6^{3-}$

Figure 15.

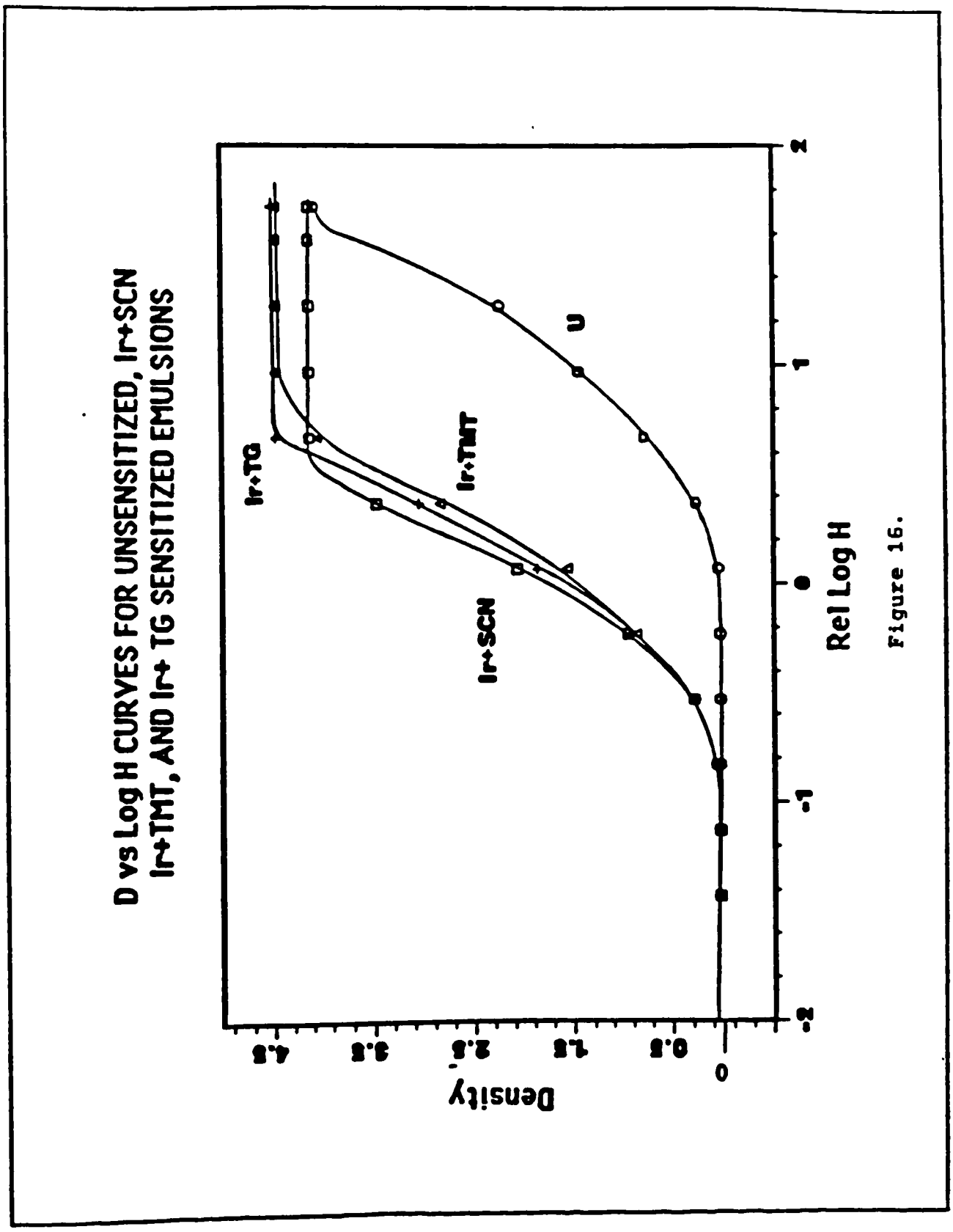

D vs Log H CURVES FOR UNSENSITIZED, Ir+SCN
Ir+TMT, AND Ir+ TG SENSITIZED EMULSIONS
Density
0
0.5
1.5
2.5
3.5
4.5
-2
-1
0
1
2
Rel Log H
U
Ir+TG
Ir+TMT
Ir+SCN

Figure 16.

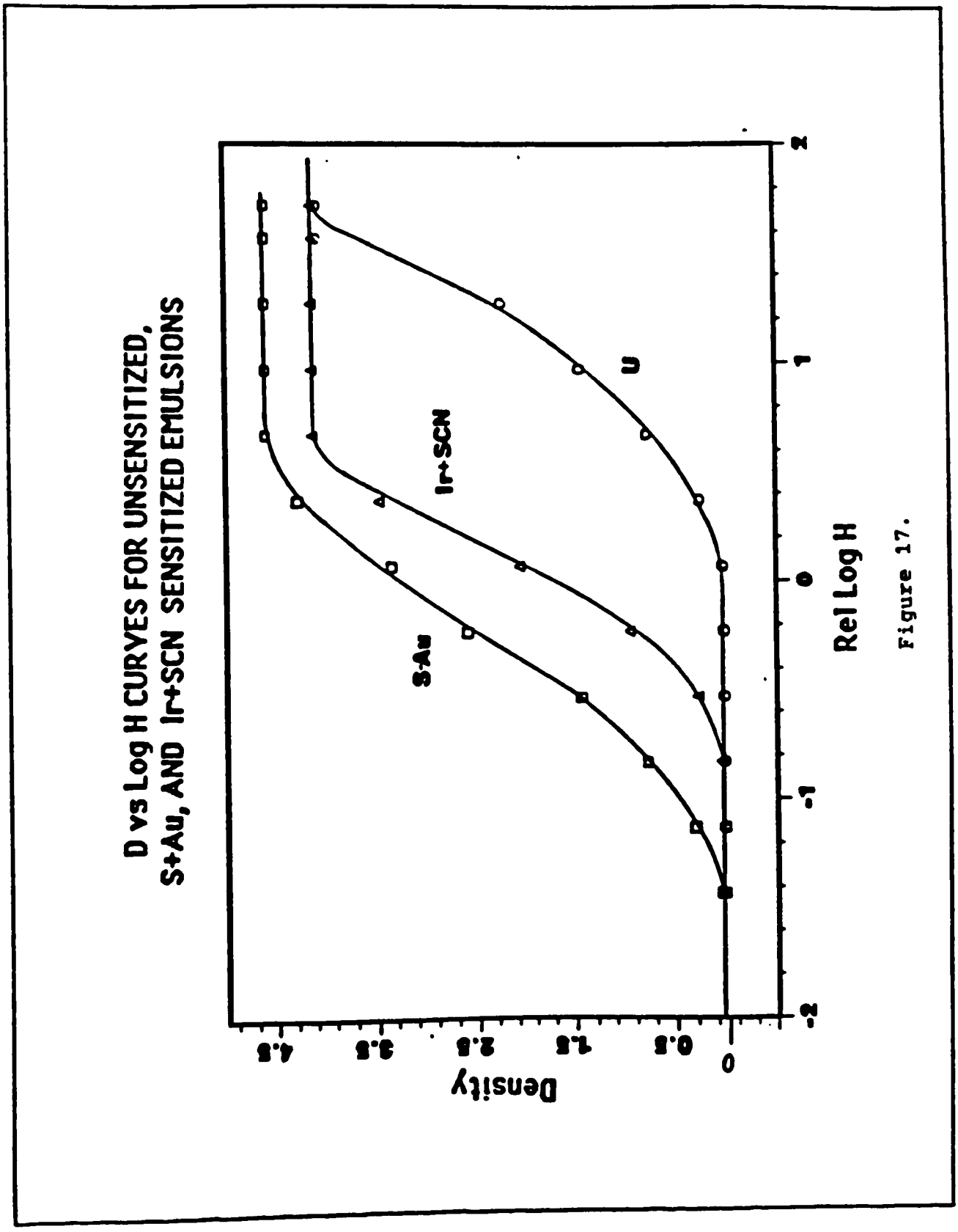

D vs Log H CURVES FOR UNSENSITIZED,
S+Au, AND Ir+SCN SENSITIZED EMULSIONS
Density
0
0.5
1.5
2.5
3.5
4.5
-2
-1
0
1
2
Rel Log H
U
Ir+SCN
S+Au

Figure 17.

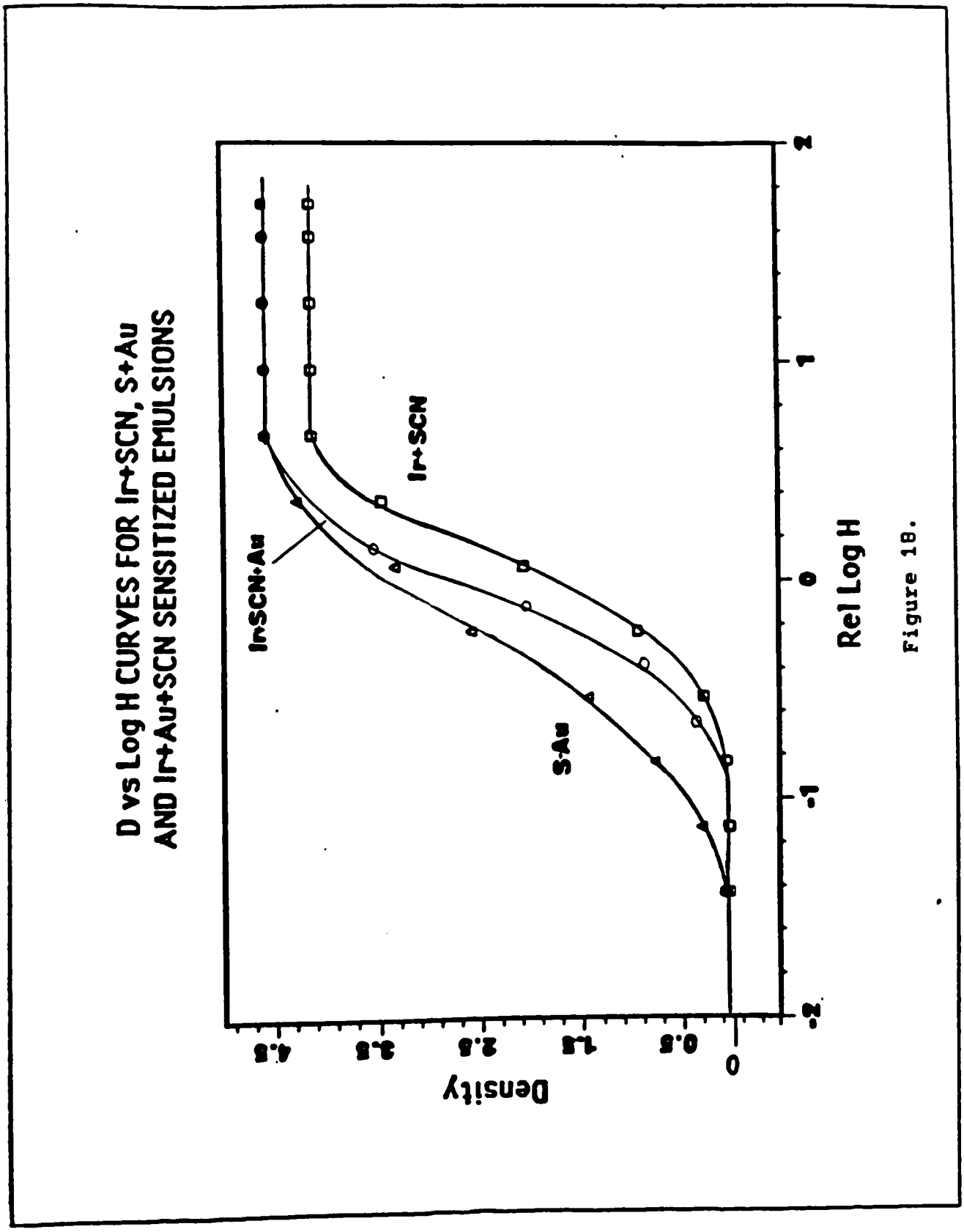

D vs Log H CURVES FOR Ir+SCN, S+Au
AND Ir+Au+SCN SENSITIZED EMULSIONS
Ir+SCN+Au
Ir+SCN
S+Au
Density
Rel Log H
0
0.5
1.5
2.5
3.5
4.5
-2
-1
0
1
2

Figure 18.

The strong desensitization produced by the thiocyanato, TMT and TG complexes could be interpreted in terms of the complex built into the crystal and acting as a deep electron trap that is not efficient for latent image formation. The final destination of the trapped electron is not known. The geometry of the proposed iridium(III) hexathiocyanato complex, would be a 6 coordinate octahedral. This geometry would make it feasible as a dopant for a AgBr crystal (fig 19). Although the calculated Δo (10Dq) value for the SCN complex is higher than that of the Br complex,[22] if it is assumed that in both cases the e_g level lies at or below the conduction band of the AgBr, the pi orbitals of the SCN and TMT ligands could provide a more stable environment for the reduction to Ir(II) (fig 20).

Another possible explanation, considering that incorporation of the Ir-S_donor complexes in the AgBr lattice would be unlikely because of the size of the ligands, is that the desensitizer is only adsorbed to the surface of the crystal and that the reduced complexes formed upon trapping of the photoelectron, undergo aerial oxidation which returns the iridium to Ir(III). Such a mechanism has been suggested by Eachus and Graves [39] for $RhCl_6^{2-}$.

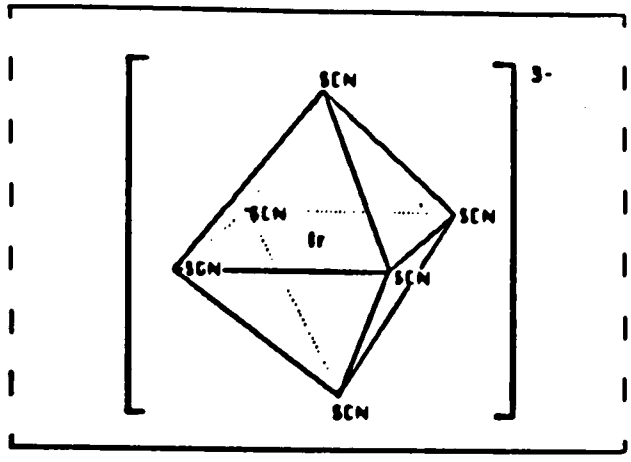


Figure 19. Proposed coordination geometry of $IrSCN_6^{3-}$

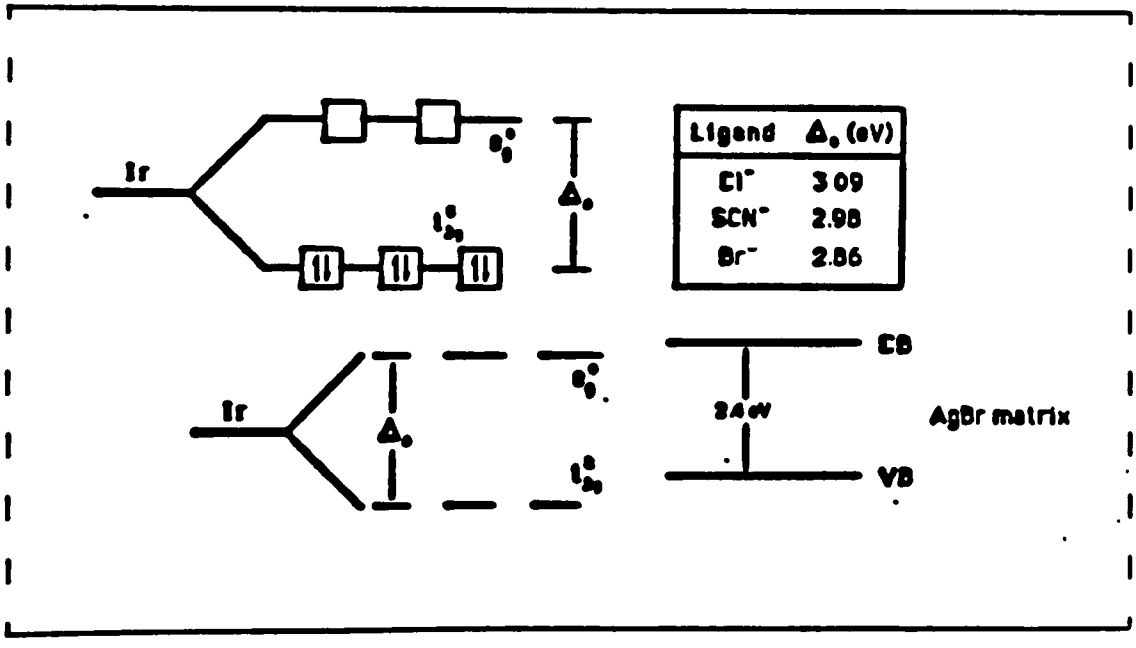


Figure 20. (a) d-d orbital splitting of the iridium hexathiocyanato complex. (b) relative position to the conduction band of AgBr.

4.3 Stability of the latent image

After latent image keeping for 3 weeks at 50°C, the unsensitized emulsion showed a 0.75 log H decrease in speed while the iridium and thiocyanate sensitized emulsion showed only a 0.08 log H decrease in speed and the sulfur gold sensitized emulsion showed no decrease in speed (table III). All latent images were completely bleached by the ferricyanide-phenosafranine bleach.

TABLE III

Decrease in speed after 3 weeks at 50°C

Unsensitized	0.75
Ir+SCN	0.08
S+Au	0.00

The resistance of the exposed Ir sensitized emulsion to attack by oxygen could indicate some form of incorporation of the Ir into the latent image. Since no evidence has been found for the existance of an Ir(I) ion in AgBr crystals sensitized with iridium, direct incorporation as iridium metal would require $3e^-$ for the reduction of the Ir(III) ion thus decreasing the quantum yield of the primary photochemical process. An alternative explanation is that in an Iridium(III)-latent image center the excess positive charge of the center associated with the latent image would create a coulombic barrier to attack on the associated silver specks by oxygen. It is also possible that the latent images are covered by a monolayer of AgBr that acts as an insulator against oxidation by oxygen but the fact that they are destroyed by the bleaching solution is evidence against this explanation of the results.

5. CONCLUSIONS

The data presented above supports the hypothesis that effective sensitization by iridium(III) requires the iridium center to be incorporated into the AgBr matrix. Thus the efficiency of sensitization can be significantly improved with the simultaneous addition of the iridium hexahalide and a silver halide solvent, such as thiocyanates, tetramethylthiourea or thiodiglycol. The efficiency of sensitization is higher for lower Gel/AgX ratios supporting the idea that iridium forms gelatin complexes which inhibit sensitization.

The experimental evidence supports a transient electron trapping rather than a hole-trapping mechanism for the observed sensitization. The increase in solarization observed for the Ir(III) sensitized emulsion when compared to the unsensitized emulsion is evidence against a hole trapping mechanism for Ir sensitization since hole trapping would decrease the solarization effect while electron trapping would tend to augment it. The decrease in optimum speed at higher concentrations is explained as dispersity of the latent image, since no increase in fog was observed. A higher increase in speed was obtained with Ir+Au in the presence of SCN than when using either Ir or Au alone with the thiocyanate suggesting additivity of Ir and Au sensitization.

Although the experiments performed showed a stabilization of iridium by thiocyanate against complexation by water and gelatin, this effect cannot be used for sensitization since premixing the Ir and the S-donor complex reduces rather than improves the intrinsic sensitivity of AgBr. The desensitizing effect is believed to be caused by deep electron trapping by an Ir-S-donor complex adsorbed to the crystal surface.

The latent image is stabilized against oxidation by the presence of the iridium centers. Since there is no evidence of incorporation of an Ir^{o} center, the stabilization can be explained in terms of the latent image associated with an Ir^{3+} center.

5.1 Ideas for future work

Although this experimental work has presented a new technique for improving the surface sensitization of silver halides with iridium complexes and has contributed new evidence for the elucidation of the mechanism of iridium sensitization, several problems remain unsolved.

The experiments performed showed a considerable increase in speed when a S- donor ligand is used as a silver solvent in the sensitization of AgBr with iridium. Whether other silver solvents such as ammonia would have a similar effect is a problem that should be addressed.

The sensitization experiments were performed on one cystal habit (octahedral) and at one pAg value. A comparison of the efficiency of this sensitization for different crystal habits should be made. The pAg dependence has been established for sulfur and gold sensitization and the latter should be investigated for iridium sensitization. The effect of the three S-donor ligands used was found to be the same for the conditions used in this work. However, at lower temperatures or at a different pAg their rates of sensitization may be significantly different.

Exposures in vacuum, photoconductivity measurements and EPR

studies must be done to better understand whether the mechanism proposed for desensitization by rhodium complexes and some desensitizing dyes applies to the iridium complexes.

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APPENDIX

PREPARATION OF $Ir(SCN)_6^{3-}$

To insure complete ligand substitution the hexachloride ion was destroyed first; this was done as follows: 2 gr. of $Na_3IrCl_6 \cdot 12H_2O$ were twice evaporated on a water bath with 5 ml of HNO_3 1:1; the residue was extracted with absolute ethanol and the red-brown filtrate was again evaporated and the crystal mass heated in a steam bath for another hour. A solution of 0.15 gr of this substance and 13.5 gr of KSCN in 40 ml of water was heated under reflux for 6 hours. A clear yellow-orange solutionwas formed which was filtered while still hot. After cooling 0.4 gr of $(n\text{-}C_4H_9)_4NBr$ in 5 ml of water were added to the filtrate, thereby orange-yellow crystals were formed which were washed with water after vacuum filtration and then dissolved in absolute ethanol at 30-35°C. This solution was filtered through activated charcoal and left standing at -10°C. Well formed crystals were obtained which were vacuum filtered with ethanol-petrol ether 1:1 and washed. The obtained substance is soluble in ethanol and acetone. Insoluble in water and ether.

CHARACTERIZATION

The IR spectrum of the compound made by Scmitke's method was taken in a Nicolet FT-IR spectrophotometer (fig 21) and that of the compound made by direct reaction of IrCl63- and KSCN was measured in a Perkin Elmer 683 with KBr pellets (fig 22). The bands observed at 2131, 2106, and 2050 correspond to the C-N stretch. The band at 880 nm corresponds to the C-S stretch and the band at 465 corresponds to the Ir-S stretch. Both spectra show good agreement with the bands reported by Schmitke. The two compounds gave also tha same UV-vis spectrum (fig 23).

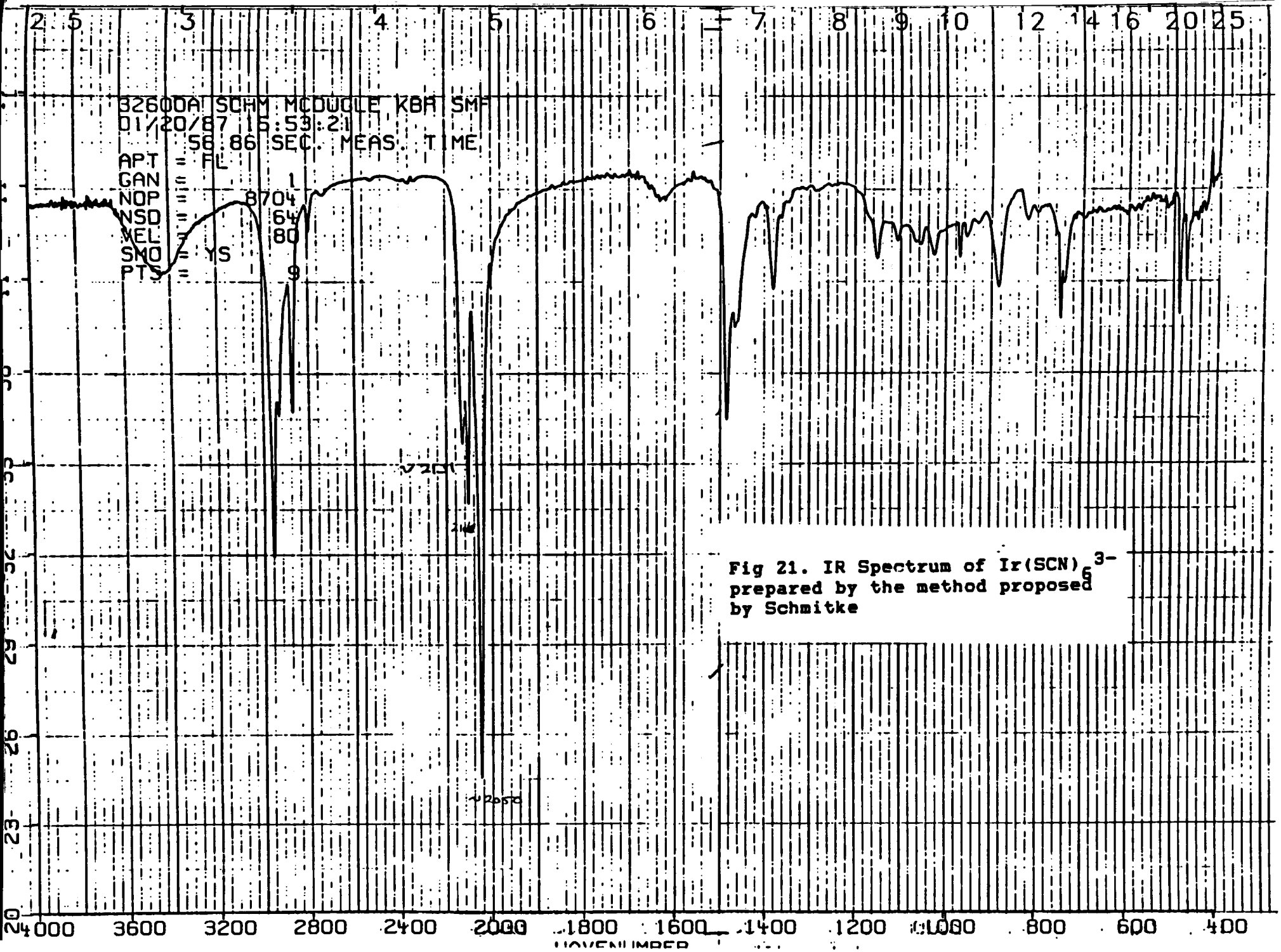

Fig 21. IR Spectrum of $Ir(SCN)_6^{3-}$ prepared by the method proposed by Schmitke

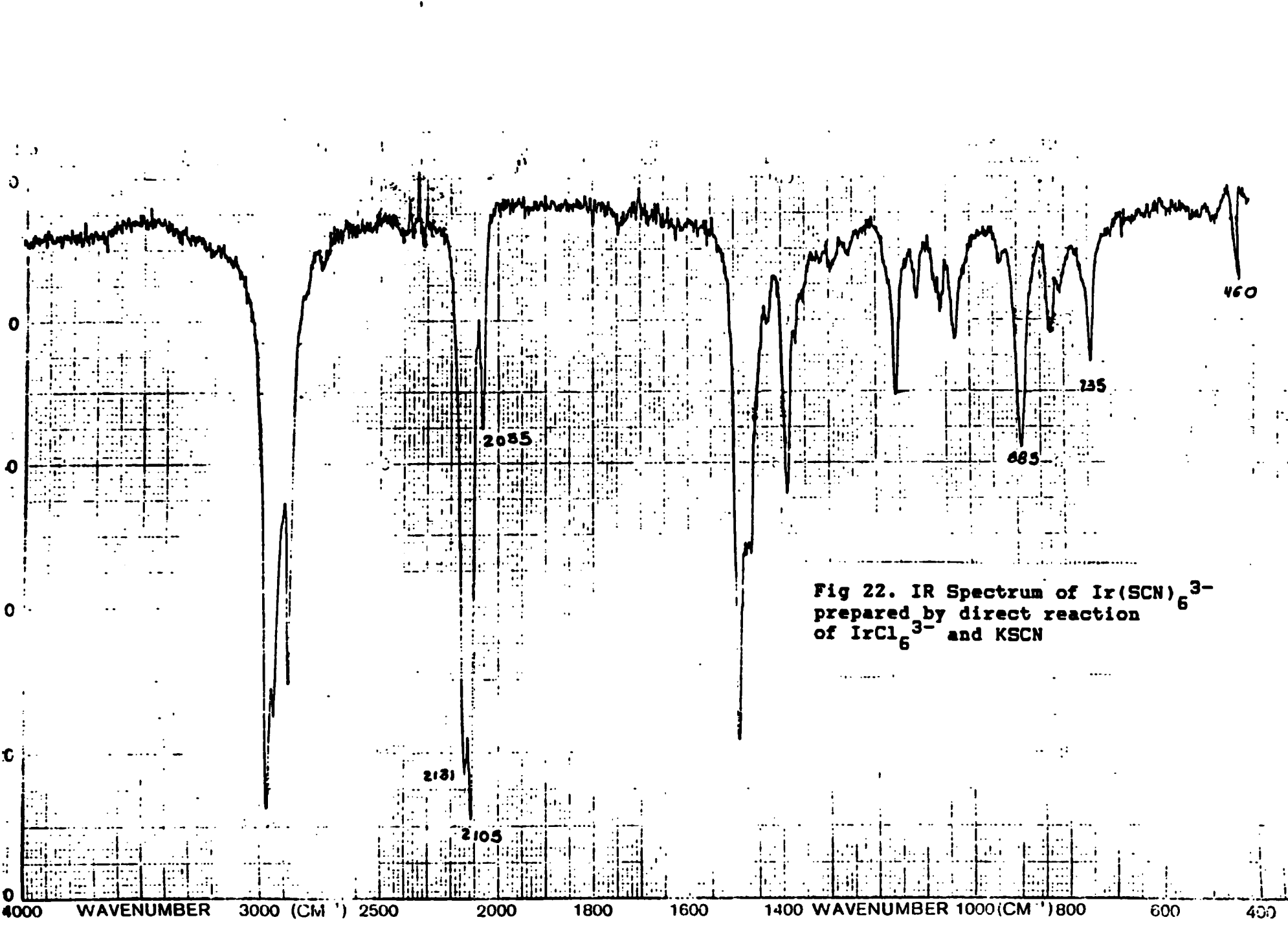

Fig 22. IR Spectrum of $Ir(SCN)_6^{3-}$ prepared by direct reaction of $IrCl_6^{3-}$ and KSCN

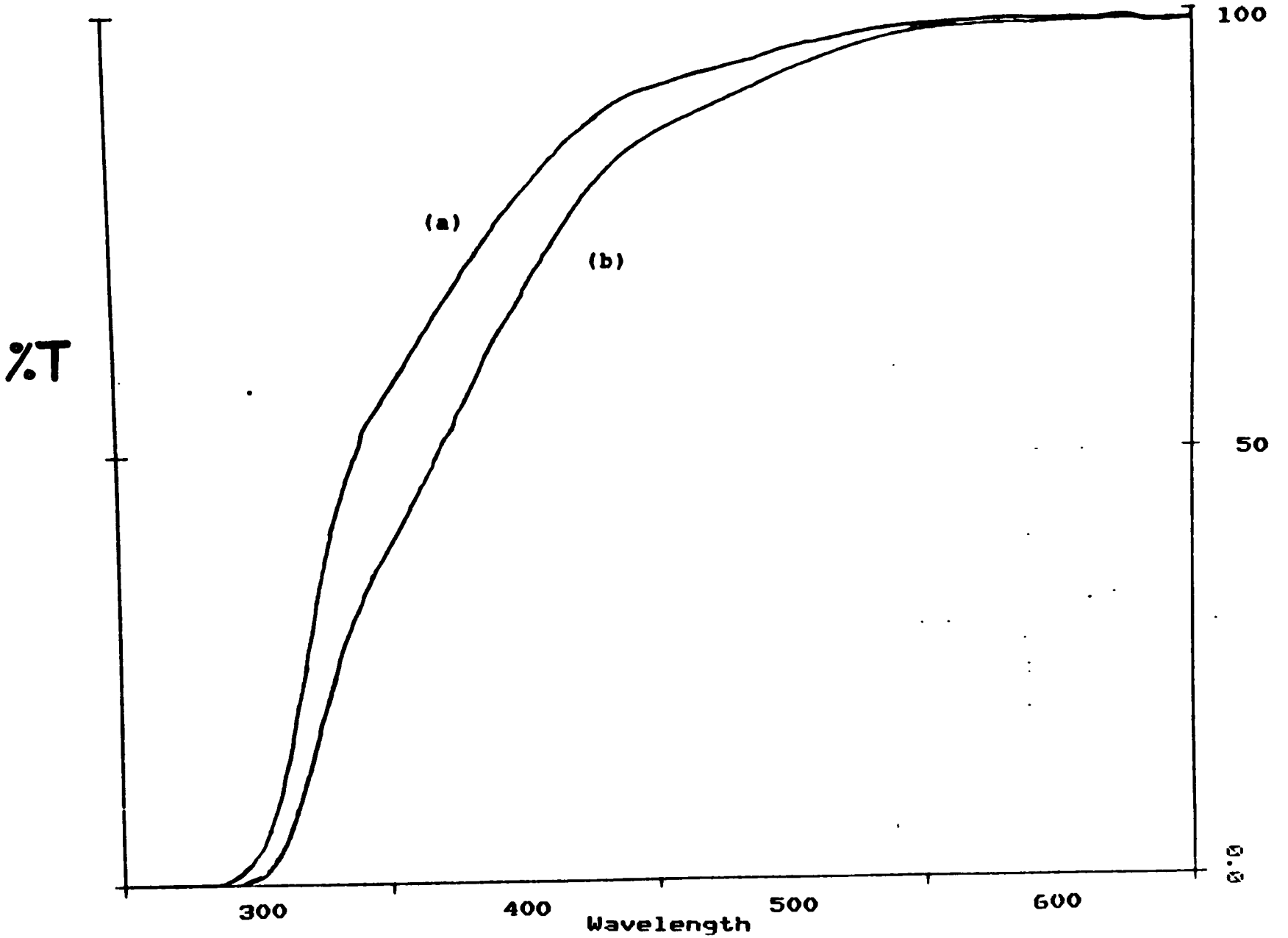

Fig 23. UV-vis Spectrum of $Ir(SCN)_6^{3-}$ prepared by the method proposed by Schmitke (a) and by direct reaction of $IrCl_6^{3-}$ and KSCN (b)

VITA

Juan Antonio Zuleta was born in Bogota, Colombia on August 25, 1956. He attended high school at Gimnasio Campestre in Bogota and completed his undergraduate work at Universidad de la Salle, where he obtained his B.S. degree in Chemistry. His senior project was on the chemistry of photographic processes. After graduation, Mr. Zuleta worked for FICOL, the Eastman Kodak facilities in Colombia as technical consultant in the quality control division and also as lecturer in seminars in basic photographic chemistry.

In May 1984 he joined the M.S. degree program in Imaging and Photographic Science at the Rochester Institute of Technology, where he completed his coursework in May, 1985 complementing his education with graduate courses in physical, organic and analytical chemistry. In May, 1986 he received the Raymond Davis Scholarship from the Society of Photographic Scientists and Engineers. The results of his graduate research were presented at the International Congress of Photographic Science in Cologne, Germany in September 1986. Mr. Zuleta is working now as adjunct faculty member in the new Center for Imaging Science at RIT where he teaches photographic emulsion and processing chemistry at the undergraduate level and is in charge of the emulsion laboratory. He is currently involved in two research projects in chemical sensitization of silver bromide emulsions.